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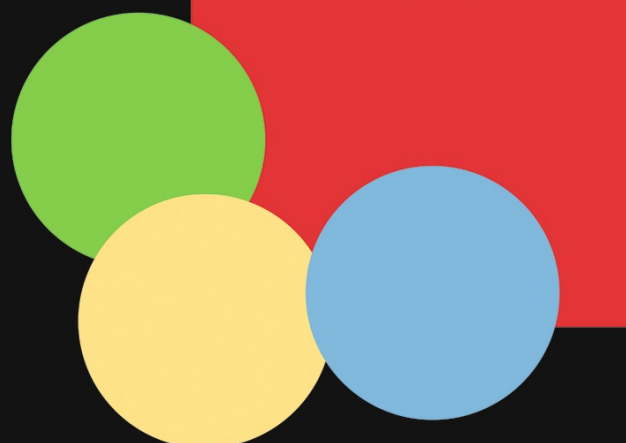
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Abstract China has relatively abundant rare earth elements (REEs) reserves and will continue to be one of the major producers of REEs for the world market in the foreseeable future. However, due to the large scale of mining and refining activities, large amounts of REEs have been released to the surrounding environment and caused harmful effects on local residents. This paper summarizes the data about the contents and translocation of REEs in soils, waters, atmosphere, and plants in REE mining areas of China and discusses the characteristics of their forms, distribution, fractionation, and influencing factors. Obviously high concentrations of REEs with active and bioavailable forms are observed in all environmental media. The mobility and bioavailability of REEs are enhanced. The distribution patterns of REEs in soils and water bodies are all in line with their parent rocks. Significant fractionation phenomenon among individual members of REEs was found in soil–plant systems. However, limited knowledge was available for REEs in atmosphere. More studies focusing on the behavior of REEs in ambient air of REE mining areas in China are highly suggested. In addition, systematic study on the translocation and circulation of REEs in various media in REEs mining areas and their health risk assessment should be carried out. Standard analytical methods of REEs in environments need to be

established, and more specific guideline values of REEs in foods should also be developed.

Keywords Rare earth element · Chinese REE mining areas · Environmental behavior

Introduction

It is widely recognized that mining activities have changed the original environmental condition and produced vast environmental problems, including ecological destruction, environmental pollution, soil erosion, and geological disasters (Aguilar et al. 2004; Klukanová et al. 1999; Liu et al. 2006; Luís et al. 2011; Salomons 1995). More toxic elements may be released into the environment and cause adverse impacts because of the disturbed environmental condition. During the last decades, a large number of studies have focused on the geochemistry of heavy metals and metalloids whose toxic effects have been well-understood in mining areas, such as As and Hg (Natarajan et al. 2006; Teng et al. 2004), whereas fewer researches have paid attention to the behavior of rare earth elements (REEs). However, with the development of mining activities and the increasing use of REEs as a new material in recent years, more studies have been paid on REEs. Several studies have indicated the harmful effects and health hazards of REEs to human beings, and it has already been proven that long-term exposure of REE dust may cause pneumoconiosis in humans (Hirano et al. 1996). In this paper, the geochemistry including several aspects, such as

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concentration, distribution pattern, and controlling factors of REEs in soils, waters, and plants in REE mining areas of China will be summarized in order to provide a better understanding of the environmental behavior of REEs.

Outline of Chinese REE resources and industry

REEs lie at the bottom of Mendeleev's Periodic Table, including 15 lanthanides, from lanthanum (La) to lutetium (Lu), scandium (Sc), and yttrium (Y). The 17 elements form a coherent group of elements with similar chemical properties. Commonly, REEs can be divided into three groups by their atomic number and masses—the light rare earth elements (LREE), the middle rare earth elements (MREE), and the heavy rare earth elements (HREE). La, Ce, and Pr are considered to be LREEs; Nd, Sm, Eu, and Gd are classified to MREEs, and those from Tb to Lu are in the group of HREEs (EPA 2012)

China has relatively abundant REE resources, and its RE reserve accounts for 23 % of world's proven reserve (18.59Mt, in 2009). The distribution of REE resources in China presents a “light north, heavy south” pattern (Anonymous 2012). LREE mines mainly exist in Baotou of the Inner Mongolia Autonomous Region, as well as in Liangshan of Sichuan province. MREE and HREE mines are located in Ganzhou of Jiangxi province. Despite of the plenty reserves, China's REE resources also show a rather high diversity in types of rare earth minerals which include bastnaesite, monazite, ion-absorption minerals, xenotime, fergusonite, and others, with a relatively complete range of REEs (Cheng et al. 2010). It is worth mentioning that the ion-absorption MREE and HREE ores are China's unique REE resources with an important position in the world (Li et al. 2010).

Since China's reform and open-door policy in 1997, China's rare earth industries have developed rapidly. 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 1,000 specifications. In 2011, China has produced over 90 % of the world's rare earth supply with the only 23 % of the world total reserves and has become to a leading producer of REEs (Anonymous 2012). However, such a large scale of mining and production

activities of REEs in China has inevitably changed the environment.

High level of REEs in China's rare earth mining areas

REEs getting “rare” in their name is because of their scattered distribution and difficulty in the refining process. The term “rare” in name of REEs do not imply that they are uncommon in nature. On the contrast, REEs are relatively abundant in the earth. The total contents of REEs exceed 200 ppm in the average crust. Some REEs are even more common than copper or lead in the crust (Castor and James 2006; Chen 2011). Table 1 shows the abundances of REEs in the upper crust.

In China, even though the background value is relatively high, REEs existing in rocks under natural conditions normally have little effects on the environment and human beings. However, in recent years, with the increased exploitation of REEs in China, mining activities have led to intensive accumulation of REEs and enhanced the level of REEs in the environment high enough to cause harmful effects on human beings (Feng et al. 2005; Husain et al. 1980). Many Chinese researches have carried out on the extent of the accumulation of exogenous REEs in China's REE mining areas.

Surface soil

REEs are naturally omnipresent in soils which are mainly originated from the weathering of local parent rocks. Under natural conditions, the concentration of REEs in soils is mainly decided by their parent rocks (Hu et al. 2006). But in REE mining areas where natural conditions have been disturbed intensively, soils always have much higher concentrations compared with their parent rocks. Concentrations of REEs in several REE mining area in China are summarized in Table 2. As shown in the Table, the total contents of REEs in soils close to mining areas are all much higher than the average values in China and in the world. Soils in Bayan Obo REE Deposit show the highest concentration of REEs which reached 27,549.58 $\mu\text{g/g}$ (Li et al. 2008). This concentration is almost 160 times higher than the average value in China. In southern REE mining areas of China, the contents of REEs are also high which range from 396 to 2,314 $\mu\text{g/g}$, and even the lowest concentration of

Table 1 The upper crust abundances of REEs (Taylor and McLennan 1985)

Element	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Th	Yb	Lu
Abundance (ppm)	30	64	7.1	26	na	4.5	0.88	3.8	0.64	3.5	0.80	2.3	0.33	2.2	0.32

REEs in the soils is twice higher than the Chinese average concentration.

Water body

Fresh water normally contains very low concentrations of REEs. The concentrations of REEs in water only range between $n \times 10^{-3} \sim n \times 10^{-1}$ $\mu\text{g/L}$ (Elderfield et al. 1990; Ji et al. 2004; Sholkvitz 1993, 1995; Sultan et al. 2009). Due to the mining activities, large amounts of REEs are released into natural water bodies in two ways: the direct discharge of industrial wastewater which contains high levels of REEs and the leaching process in soils which are enriched in REEs. As a result, concentrations of REEs in water bodies have been significantly enhanced. Yellow river, the second biggest river in China, is the best example (He et al. 2004a, b, c). Baotou city where Bayan Obo REE

Deposit is located is famous for its REE industry. The Baotou section of the Yellow River received most of the wastewater from REE industries in Baotou. Table 3 shows the concentration of REEs in the mainstream and two branches (Kundulun River and Sidaosha River) of Baotou section of the Yellow River. It can be seen from Table 3 that the concentrations of REEs in surface water, as well as the suspended particles and surface sediment in Baotou section of the Yellow River, are all significantly higher than the average value of rivers in North China (Zhou et al. 2012). The mainstream had the lowest total REE concentration in comparison with the two branches. Sidaosha River had the highest level of REEs. The total concentration of REEs in suspended particles and surface sediments of Sidaosha River are 31,524 and 30,461 $\mu\text{g/L}$, respectively. Both of them are almost 200 times higher than the average value of rivers in North China.

Table 2 Concentrations of REEs in soil samples in REE mining areas of China (micrograms per gram)

Place	Jiangxi REE mining areas					Baotou REE mining areas		China average	World average
pH	—	5.26	3.69	4.13	4.30	7.02	7.02	—	—
La	208.50	62.3	110	492	30	6,905.24	55.03	37.4	50
Ce	351.63	85.2	44.2	630	49	12,169.89	132.60	64.7	7
Pr	46.90	—	31.3	166	11	1,614.28	12.02	6.67	35
Nd	159.75	97	154	411	39	5,726.56	42.93	25.1	4.5
Sm	24.98	39.0	49.1	127	21	492.35	6.70	4.94	1
Eu	2.36	1.50	3.99	12	1	96.90	1.25	0.98	4
Gd	21.68	—	42.3	106	21	329.15	5.43	4.38	0.7
Tb	2.54	10.2	6.64	13	4	38.06	0.76	0.58	5
Dy	11.09	—	37.4	42	21	54.63	4.37	3.93	0.6
Ho	1.97	—	7.28	16	7	—	0.91	0.830	2
Er	5.47	—	19.7	33	17	—	2.54	2.42	0.6
Tm	2.87	—	2.45	7	3	—	0.38	0.35	3
Yb	4.58	36.7	15.9	27	20	—	2.53	2.32	0.4
Lu	0.68	5.60	1.91	6	3	—	0.40	0.35	40
Y	51.23	—	—	—	—	—	—	—	—
ΣREE	869.73	542	688.2	2314	396	27,549.58	279.84	176.8	193.8
Reference	Zhu et al. (2002)	Gao et al. (2001)	Yu et al. (2009)	Wei et al. (2002)	Wei et al. (2002)	Li et al. (2001)	Zhang et al. (2012)	Wei et al. (1991)	Wang et al. (1989)

Table 3 Concentrations of REEs in Huanghe River (Baotou section)

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	ΣREE
Dissolved REE(μg/L) ^a															
Yellow river (main stream)	0.10	0.22	0.034	0.095	0.054	0.018	0.028	0.006	0.08	0.014	0.03	0.007	0.032	0.006	0.80
Kundulun River	140	152	16.08	52.01	6.91	1.52	7.22	0.88	3.80	0.18	2.34	0.24	1.48	0.21	406
Sidaosha river	988	1,149	294	1,193	62.35	5.59	67.33	5.58	9.08	1.35	9.79	0.36	1.92	0.22	3,826
Southern river average ^b	0.065	0.135	0.014	0.065	0.014	0.016	0.011	0.002	0.011	0.003	0.014	0.002	0.013	0.002	0.367
Suspended matter (μg/g) ^c															
Yellow river (main stream)	33.16	68.26	8.47	28.70	5.79	1.31	6.29	0.82	3.39	0.77	2.25	0.25	1.76	0.25	161
Kundulun River	86.16	139.3	15.8	51.98	6.61	1.20	4.31	0.97	1.87	0.68	1.36	0.22	1.01	0.22	312
Sidaosha river	7,746	14,472	1,162	6,901	478	98.59	423	63.38	88.03	12.32	33.45	5.63	35.21	5.28	31,524
Southern river average ^b	40.07	71.50	8.41	30.80	5.36	1.03	4.72	0.71	3.31	0.67	1.78	0.28	1.68	0.88	171.26
Sediment (μg/g) ^d															
Yellow river (main stream)	27.47	55.94	6.74	24.20	4.48	0.9	4.15	0.50	2.50	0.50	1.50	0.14	1.30	0.16	130
Kundulun River	50.77	116.6	13.30	47.00	7.04	1.26	6.79	1.01	3.52	0.73	2.01	0.24	1.18	0.22	251
Sidaosha river	7,823.0	14,074	1,403	5,919	497	99.3	423	43.5	82.4	8.97	38.6	6.06	38.3	5.98	30,461
Southern river average ^b	51.00	94.00	11.50	41.00	7.60	1.29	6.81	1.10	5.90	1.19	3.37	0.57	3.51	0.55	229.70

^a He et al. (2004a)^b Zhou et al. (2012)^c He et al. (2004b)^d He et al. (2004c)

Additionally, it is well known that the concentrations of dissolved REEs in water under natural environment are limited which are often ignored (Ding et al. 2005a; Wang et al. 2000b). However, the total concentrations of dissolved REEs in rivers near REE mining areas in China are about three orders of magnitude higher than those in other natural rivers which are not affected by mining activities worldwide (Table 4).

Leaching process in soils is another important pathway for exogenous REEs entering water bodies which could cause contamination in groundwater, especially in southern REE mining areas of China. The highest reported REE concentration in well water in Chinese mining areas is 130 μg/L which occurred in one of the exploratory mine of Shandong REE mining areas (Lu et al. 1995). Except for that extreme value, other reported REE concentrations in well water were not too high. Several published results of REE concentrations in groundwater are listed in Table 5. Even though the total concentrations in groundwater are not too high when compared with Baotou section of the Yellow River mentioned earlier, it

could lead to even worse effect because they are sources of drinking water for local people.

Atmosphere

Along with intensive worldwide use of REEs, an increasing amount of REEs has been emitted into atmosphere. Unfortunately, unlike in soils and water bodies where the contents of REEs have been widely studied, the levels of REEs in the air have not received enough attention. In general, existing studies have investigated three aspects: (1) the long haul transport of REEs from continents to oceans (Arimoto et al. 1989; Sholkovitz et al. 1993; Sholkovitz 1994a; Yang et al. 1993); (2) airborne particulate matter in urban areas and levels of REEs in the air (Chen et al. 1985; Hong et al. 2010; Suzuki et al. 2011; Wang 2003); and (3) air pollution caused by REEs in forms of ambient particles produced during the cracking and combustion of oil in the vicinity of refinery factories because of the fact that many petroleum-cracking catalyst and products are highly enriched in the LREEs (La, Ce,

Table 4 Concentration of dissolved REEs in rivers

μg/L	River's name	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	ΣDREE
Mining areas	Ganjiang River ^a	2.412	0.022	0.060	0.051	0.013	0.007	0.093	0.004	–
	Huanghe River (Baotou section) ^b	0.10	0.22	0.095	0.054	0.018	0.006	0.032	0.006	0.800
	Zhujiang River (Guangzhou section) ^c	0.035	0.075	0.050	0.037	0.015	0.010	0.023	0.005	0.246
Natural areas	Changjiang River ^d	0.050	0.110	0.070	0.013	0.004	0	0.008	0.002	0.261
	China's average ^e	0.060	0.120	0.060	0.010	0.005	0.003	0.008	0.002	0.268
	Amazon River ^f	0.074	0.212	0.127	0.035	0.008	–	0.015	–	–
	Indus River (ng/L) ^g	2.91	2.41	3.20	0.71	0.22	–	0.94	0.17	–

^a Meng et al. (2007)^b He et al. (2004a)^c Wang et al. (1998)^d Zhang et al. (1992)^e Wang et al. (1995)^f Hu and Jin (2000)^g Meng et al. 2008

and Nd) (Brown et al. 1991; Kitto et al. 1992; Olmez et al. 1985). There were only two studies about the REE mining areas, and both of them were carried out in Jiangxi province, China. Published results of REE concentrations in the air are listed in Table 6.

Additionally, considering the adverse effects of atmospheric REEs on human beings, Zhu et al. (1996) investigated the concentrations of inhalable REEs in the air in an ion-adsorbed REE mining area in Jiangxi province. The results revealed a much higher level of REEs in inhalable particles in the mining area of 612.5 ng/m³ in comparison with REEs concentration in total suspended particulates in the same area of 359.1 ng/m³, indicating negative health effects on local residents.

Plant tissues

REEs are not essential elements to plants. However, plants can absorb REEs from soils through roots and can also uptake REEs via leaves exposed to atmospheric particles containing REEs mainly from REEs mining

areas (Ichihashi et al. 1992; Tyler 2004; Volokh et al. 1990). The concentrations of REEs in common plants are generally low under natural conditions, normally around 10⁻³–10⁻¹ μg/g (dry mass) (Wang et al. 1997). But in the REE mining areas of China, both soils and water bodies have high levels of REEs as a result of mining activities as previously mentioned. Therefore, much attention has been paid on the investigation of the REE levels in plants grown in REE mining areas.

Table 7 lists the REE concentrations in several previously investigated plants in REE mining areas of China. The results show that the level of REEs varied in different species of plants. Green stuff and sweet potato had high REE concentrations which are 10–20 times higher than the maximum limited levels of contaminants in foods issued in National Standards GB 2762-2005 (Chinese Ministry of Health 2005). The total concentrations of REEs in all the other plants in the REE mining areas were lower than the limited level.

Researchers have also carried out studies on REE hyperaccumulating plants in order to find a feasible

Table 5 Concentrations of REEs in groundwater in REE mining areas of China (micrograms per liter)

Location	Deposit type	REEs mining areas	Control areas	Method	Reference
Jiangxi	Light REE	15.2±5.6	7.0±3.7	Spectrophotography	Lu et al. (1995)
Jiangxi	Heavy REE	8.4±5.9	5.6±2.2		
Shandong	Light REE	5.1±2.6	3.2±0.8	ICP-MS	Zhu et al. (2002)
Jiangxi	Light REE	9.18±5.82	0.38±0.28		

Table 6 Concentrations of REEs in TSP

ng/m ³	Non-mining areas				REE mining areas	
	Delft, Germany	Osaka, Japan	Beijing, China	Jiangxi, China	Jiangxi, China	Jiangxi, China
Sampling location						
La	0.504	6.48	17.03	20.8	1,210	120.1
Ce	0.592	10.62	38.7	29.5	115	43.8
Pr	0.109	1.368	4.09	4.5	–	26.5
Nd	0.345	3.24	13.50	17.0	830	91.0
Sm	0.0635	0.468	2.82	2.7	119	17.1
Eu	0.0182	0.0378	0.59	0.3	125	1.9
Gd	0.0698	0.378	2.57	2.3	–	14.5
Tb	0.0084	0.0378	0.33	0.3	13.30	1.8
Dy	0.0460	0.342	1.63	1.4	–	8.3
Ho	0.0086	0.0594	0.29	0.2	–	1.2
Er	0.0234	0.1296	0.82	0.6	–	3.2
Tm	0.0030	0.01368	0.11	0.0	–	0.3
Yb	0.0235	0.135	0.65	0.5	13.5	2.0
Lu	0.0027	0.027	0.09	0.0	24.2	0.3
Y	0.294	–	3.28	6.5	–	27.3
ΣREE	4.35	23.39	94.65	86.6	2,450	359.1
Method	ICP-MS	SSMS	ICP-MS	ICP-MS	–	ICP-MS
Reference	Wang et al. (2000a)	Sugimae (1980)	Wang et al. (2001a)	Zhu et al. (2003)	Peng and Wang (1995)	Zhu et al. (2003)

way to remediate REE-contaminated soils. REE hyperaccumulators can accumulate much higher contents of REEs, especially in their aboveground parts. The REE contents in the aboveground parts of plants are usually used as an indicator in the identification of REE hyperaccumulators which need to be higher than 1,000 µg/g (dry mass) (Garbisu et al. 2001). According to the criterion, four species have been widely recognized as REE hyperaccumulators (Table 8).

In those four REE hyperaccumulators, *Dicranopteris dichotoma* is the most general and important REE

accumulating plant in REE mining areas in China which has been considered as an ideal material on the study of REE behavior in plants for many years (Wei et al. 2006). In China, Li et al. (1992) first found that *D. dichotoma* could accumulate REEs in southern part of Jiangxi province and reported the contents of REEs in different parts of *D. dichotoma*. Since then, Chinese scholars have been carrying out lots of researches on contents, forms, and distribution of REEs inside *D. dichotoma*. Several published results focusing on *D. dichotoma* grown in Chinese REE mining areas are summarized

Table 7 Concentrations of REEs in plants

Plant	REE mining areas	Maximum limited level in food issue	Method	Reference
Green stuff average	7.54	≤0.7	ICP-MS	Zhu et al. (2002)
Sweet potato	13.59	≤0.5	Spectrophotography	Zhang et al. (1999)
Rice	1.55	≤2.0	Spectrophotography	Zhang et al. (1999)
Peanuts	0.36	≤0.5	Spectrophotography	Zhu et al. (1997)
Navel Orange	0.254	≤0.7	ICP-MS	Yu et al. (2009)
Tea leaf	1.59	≤2.0	ICP-MS	Zhang et al. (1997)

Table 8 Concentrations of REEs in leaves of four typical REE hyperaccumulator plants (micrograms per gram)

Latin name of plant	Family of plant	Max. contents of REEs in leaves	Reference
Mockernut hickory	Juglandaceae	1,350	Thomas (1975)
<i>Cary tomentosa</i>	Juglandaceae	2,296	Robinson (1943)
<i>Blechnum orientale</i>	Blechnaceae	1,022	Xiao et al. (2003)
<i>Dicraneopteris dichotoma</i>	Gleicheniaceae	3,358	Xiao et al. (2003)

in Table 9. Obviously, concentrations of REEs in leaves are in a high level.

In summary, based on existing research results, we briefly present the biogeochemical cycle of REEs in Chinese REE mining areas (see Fig. 1). The range of total REE contents in different environmental media varied considerably. The levels of REEs in REE mining areas of China are obviously higher than those in non-mining areas.

Translocation of REEs in REE mining areas of China and influencing factors

The translocation of REEs in various environmental compartments has gained considerable attention world widely over the last decade (Hu et al. 2006; Milliman et al. 1983; Sholkovitz 1994b; Tyler 2004). But this interest is based on the increasing applications of REEs as tracers of geochemical processes and most of the researches were carried out in natural waters, coal mines, and other mineral areas (Eskenazy 1999; Protano et al. 2002).

However, with the growing amount of experimental results which indicated harmful effects of REEs on human beings, it is important to focus on the toxic effects of REEs, especially in REE mining areas. Investigations have been carried out on forms, distribution, and fractionation of REEs in soils, waters, atmosphere, and plants in different REE mining areas in China. Although all those published results are important for a better understanding of translocation of REEs in special areas, there is still lack of integrity and comparability.

Forms of REEs in Chinese mining areas

It is widely recognized that toxicity of heavy metals does not merely depend on the total concentrations but on their forms (Brummer 1986). Forms of REEs are directly related to their mobility, distribution, bioavailability, and ultimate fate in the environment (Ji et al. 2004). REEs are a group of elements which are relatively inert. As a result, REEs mainly exist in residue form in soils, sediments, and suspended particulates in water bodies in China with very low mobility.

Table 9 Concentrations of REEs in *Dicraneopteris dichotoma* (micrograms per gram)

		Soil	Root	Stem	Petiole	Lamina	Method	Reference
Mining areas	1	330.68	926.43	137.63	136.66	2,648.79	ICP-MS	Wang 2005
	2	207.02	861.84	106.18	57.76	2,090.30	ICP-MS	Wang 2005
	3	431.8	559.0	289.0	–	3,263.8	ICP-AES	Li et al. (1992)
	4	806.4	955.9	287.0	–	2,825.8	ICP-AES	Li et al. (1992)
	5	2,373	1,570	459	102	2,271	ICP-MS	Wei et al. (2001)
	6	396	1,269	401	61	977	ICP-MS	Wei et al. (2001)
	7	2,314	1,754	633	56	1,660	ICP-MS	Wei et al. (2001)
	8	–	788.79	170.05	–	1,030.33	ICP-AES	Hong et al. (1999)
Non-mining areas	1	–	851.32	98.64	40.74	1,494.45	ICP-MS	Wang et al. (2010)
	2	15.3	38.7	39.5	–	1,914.0	ICP-AES	Li et al. (1992)
	3	111	134	107	51	1,121	ICP-MS	Wei et al. (2001)

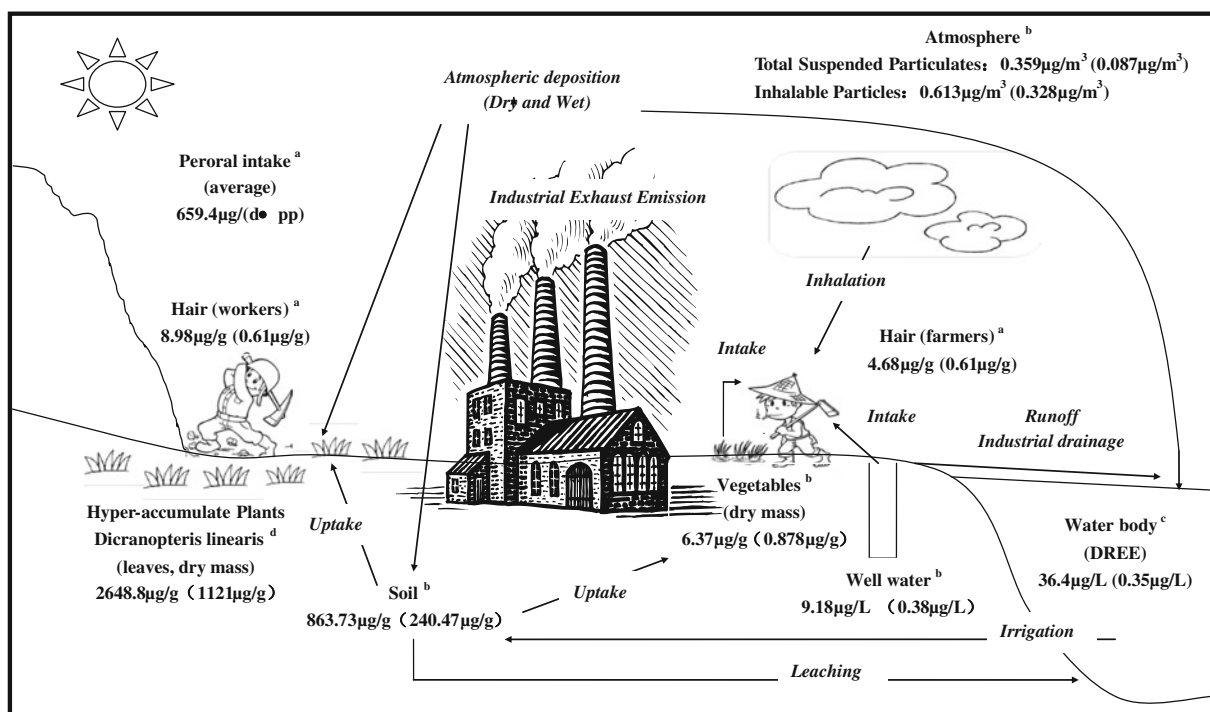


Fig. 1 The average contents of REEs in Chinese REE mining area. *a* Lu et al. (1995), *b* Zhu et al. (2002), *c* Meng et al. (2007), *d* Wei et al. (2001)

However, in REE mining areas, the forms of REEs present significantly different features. Organically bound and exchangeable REEs are considered as the predominate forms in soils in REE mine areas of China (Gao et al. 2001; Yu et al. 2009; Zhang et al. 2012). Wei et al. (2001) determined content of soluble REEs in soils (extracted by 1.0 mol/L NaAc-HAc, pH=4.8) which could be used directly by plants in Jiangxi REE mining areas. They found that soluble REE concentrations accounted for 44–52 % of the total REE concentrations in the mining areas, whereas in non-mining area, the ratio was only 14 %.

Although it has been found that residue form still accounted for the largest part of REEs in sediments and suspended particulates, noticeably increasing proportions of exchangeable REEs were observed (He et al. 2004a, b, c). All of those results indicated obviously higher mobility and bioavailability of REEs in Chinese REE mining areas.

High mobility of REEs in the mining areas leads to high plant availability. Plants grown in REE mining areas, especially REE hyperaccumulators, contain a high level of REEs in their organs. *D. dichotoma*, one of REE hyperaccumulator and dominant species in

Chinese REE mining areas, was frequently used as ideal materials for studies on REE forms inside plants. But owing to the lack of sensitive instruments and practical analytical techniques which allow speciation analysis of REEs in biological materials, investigations on forms of REEs inside plants are still limited. Guo et al. (1996) separated two kinds of REE-bound proteins in leaves of *D. dichotoma*. Wang et al. (2001b) studied REE speciation in *D. dichotoma* (DD) by molecular activation analysis (MAA). The results showed that the REEs were firmly bound to the proteins, polysaccharides, and DNA in the leaves of DD. Zhang et al. (2000a) separated leaves of *D. dichotoma* collected from a rare earth ore area into ether fractions, water fractions, base fractions, and residues and determined the contents of REEs by instrumental neutron activation analysis (INAA). They found most of REs remained in the residues (pectin, hemi-cellulose, and cellulose).

Distribution characteristics of REEs in Chinese mining areas

The distribution of exogenous REEs in the environment of REE mining areas is an important aspect of

REE geochemical behavior. Under natural conditions, the translocation ability of REEs is relatively weak as compared with other metal ions. A vast majority of the exogenous REEs are fixed on solid surfaces and exist in inert forms, which are normally concentrated in the top layer of soils or deposited in sediments in water bodies (Jones 1997).

However, areas around REE mining sites are usually overloaded with REEs. The forms of REEs varied with the change of environment. Studies revealed that REEs had high mobility in soils in Southern REE mining areas of China. The strong weathering and low pH value in soils are considered as the main reasons (Ma et al. 2004; Xu 2005). High proportions REEs have also been found in dissolved forms or absorbed by suspended particulates in the mining areas as compared to natural water bodies (He et al. 2004b; Meng et al. 2008), which also indicate a strong mobility of REEs in areas around mining sites.

After uptaking by plants, REEs may enter different parts of plants. It has been observed that, under natural conditions, 80 % REEs are retained in roots and the concentrations of REEs in plant organs are always ranked in the order of root>stem>leaf>flower>fruit and seed (Ji et al. 2004; Yang 1996). Tagami and Uchida (2005) measured REE contents in plant organs cultured in REE-contained nutrient solution for 1 day by ICP-MS. They found that almost all of the absorbed REEs were distributed in fine roots and only small amounts of REEs were found in leaves. Feng et al. (2001) and Zhang et al. (2002) observed similar results in their researches.

However, a totally opposite result has been found in hyperaccumulating plants grown in REE mining areas. REEs uptaken by REE hyperaccumulators in the mining areas are distributed mainly in their aboveground parts. Studies demonstrated the \sum REEs in *D. dichotoma* grown in the mining areas followed the order of leaf= root>stem>petiole (see Table 9). In addition, the age of leaves may also be a factor influencing REE distribution in plants. Xiao et al. (2003) determined REE contents in fern collected in South China by INAA, and the results showed that the older the leaves were, the higher REE concentrations they had.

The distribution of REEs in plant organs at the cellular level is another hot topic. The limitation of analytical procedure has made it hard to locate REEs in plant cells. Some of the results are even contradictory, especially when they refer to whether lanthanides

can pass through cell membranes. It is generally considered that REEs are fixed on the cell walls of plants mainly because of the strong absorbance by ionogens with negative charges on cell walls, such as carboxyl and hydroxyls (Han et al. 2005; Shan et al. 2003). In addition, the precipitation with phosphate in the cell gap could lead to a further difficulty for REE ions entering into cell membranes (Diatloff et al. 1993; Quiquampoix et al. 1990; Robert et al. 1996). However, with the development of the analytical methods in recent years, more and more results indicated that even though it is difficult, REEs ions may pass through cell membranes. Li et al. (1995) found that Ce could enter plant cells and especially be accumulated in cell nucleus determined by EDX. Zhang et al. (2000b) determined REE contents in protoplasm of plants from REE mining areas by MAA and found REEs could enter cells. Gao et al. (2003) revealed that Eu and La existed in cytoplasm and were bond to chloroplast, mitochondria, and cell nucleus. Additionally, studies demonstrated that REEs could possibly be involved in plant growth activities. Hong et al. (1999) indicated that La could replace magnesium in the structure of chloroplast. Wei et al. (2000) demonstrated the same result in their study using EXAFS.

Fractionation of REEs in Chinese mining areas

It is known that all 15 REEs share similar properties, but they still have differences from each other. As a result, REE fractionation may take place during the transport processes. REE patterns in soils, suspended particulates, and sediments exhibit a light REE enrichment and negative Eu anomaly in REE mining areas of Northern China (He et al. 2004a; Li et al. 2008) and a heavy REE enrichment pattern with strong negative Eu anomaly in REE mining areas of Southern China (Gao et al. 2001; Yu et al. 2009). Results of these studies revealed that in soils and water bodies, the distribution patterns of REEs are all in line with their parent rocks. No obvious fractionation between REEs occurred during those transport processes.

However, a significant fractionation phenomenon among individual members of REEs were observed during the transport processes from soil to plant, as well as the transportation inside plants (Miekeley et al. 1994; Shan et al. 2003). Previous studies had indicated several kinds of REE enrichment features in plant and

the LREE-enrichment in the aboveground part was considered as the most common one in general. However, Ding et al. (2005b; 2007) observed heavy REE enrichment in leaves, light REE enrichment in roots, and middle REE enrichment in stems in their hydroponic experiment on *Triticum aestivum* L. and *Glycine max* L. Wang et al. (2005) found a light REE depletion in the aerial parts of *Oryza sativa*. Furthermore, the tetrad effect caused by anomaly of individual REE elements was also demonstrated in several researches (Feng et al. 2002; Wyttenbach 1998). Several possible mechanisms of REE fractionation in plants have been discussed, including organic ligands bonding in rhizosphere, cell wall absorption, and P precipitation in cell gaps. Different mechanism may influence different stage of REE transportation from soil to various parts of plants. Liang et al. (2008) had a thorough discussion on the REE fractionation mechanisms in plants in their review and developed a conceptual model of fractionation of REEs in plants.

Unlike characteristics of REE fractionation in plants, the light REE enrichment can be regarded as the representative feature of REEs in atmospheric particles whether in REE mining areas or not according to existing studies. La, Ce, Pr, Nd, Sm, Eu, and Y share almost 90 % of total atmospheric REE burden. The ratio of light REE to heavy REE and the ratio of light REE to total REE in atmospheric particles collected from different areas are presented in Table 10. The value of LREE/HREE in Chinese REE mining areas are 9.51 which is far above this ratio in local soils (2.26) (Gao et al. 2001).

Influencing factors

Same as under natural conditions, the behavior of REEs in REEs mining areas are influenced by many factors, such as their parent rocks, weathering processes, soil-

forming processes, climate, pH value, redox conditions, and organic matters (Cao et al. 2001; Heinz et al. 1993; Sholkovitz 1994b). Among these factors, pH value strikingly plays an important role in controlling translocation of exogenous REEs in the environment. Literature data suggested a strong negative significant correlation between pH value and REE mobility in the environment. The reason is that high pH value could significantly enhance the absorption of REEs, thus decreasing their mobility. Zhu et al. (1996) compared REE migration in soils under different pH conditions using numerical simulation and isotopic tracer. The results revealed that the migration distance turned out to be 1 cm for acid soils annually, 0.5 cm for slight acid soils annually, and no migration for the alkaline soils. Ran and Liu (1992) found increasing desorption of REEs from 29.5 to 90 % when pH decreased from 6.3 to 4.1. Zhu et al. (1993) also demonstrated that the adsorption of REEs was much greater in soils of higher pH due to the formation of complex ions (such as $\text{Ln}(\text{OH})_2^{2+}$, $\text{Ln}(\text{OH})_2^+$, and $\text{Ln}(\text{OH})_4^-$) and their strong absorption at the sites covered with OH^- . pH can influence REE behavior by controlling the presence and concentrations of metal ions in water body. The concentrations of REEs in water decrease significantly when the pH increases. The reason is the occurrence of the coagulation and precipitation of Fe–Al–Mn oxides/hydroxides which can effectively absorb and remove REEs from water.

Oxidization and reduction conditions mainly control the behavior of Ce and Eu because of their changeable valence (Braun et al. 1990; Ma et al. 2004). Under normal conditions, all REEs exist as +3 ions except that Ce and Eu also occur as Ce^{4+} and Eu^{2+} , respectively. Thus, Ce and Eu could be separated from the other REEs with the changes of redox conditions. Under oxidation conditions, Ce occurs as Ce^{4+} which is relatively inert and could be stabilized by forming oxides or by adsorption onto solids, thus causing a significant positive Ce anomaly.

Table 10 The fractionation features of REEs in atmospheric particulate matters

Sampling location	Non-mining areas				REE mining areas
	Delft, Germany	Osaka, Japan	Beijing, China	Jiangxi, China	Jiangxi, China
LREE/HREE	11.06	19.83	11.47	14.11	9.51
LREE/ Σ REE	0.90	0.952	0.920	0.863	0.837
Reference	Wang et al. (2000a)	Sugimae (1980)	Wang et al. (2001a)	Zhu et al. 2003	Zhu et al. 2003

Conclusions

After reviewing the collected data, we found that with the sharp increase of mining and producing activities, the environment of mining areas in China has dramatically changed in the past decades. Large amount of REEs released into the environment, scattered, and accumulated in soils, waters, atmosphere, and plants nearby through various transport processes. Results from various studies focusing on the contents of REEs in mining areas all showed a significantly high level of REE in every environmental component of mining areas, which was hundreds of times higher than non-mining areas. Furthermore, due to special mining environmental conditions, such as low pH, the behavior of REEs in mining areas presented differences from them in natural conditions. Comparing with natural conditions, REE existed in more active states in mining areas, such as exchangeable REEs in soils and dissolved REEs in water bodies. Those REEs were easier to move and transport among different environmental components, as well as to be intake by plants and enter into food chains which indicate possible harmful effect on human. Previous studies have already pointed out the accumulation of REEs inside local residents' bodies which could be a threat to their health.

However, studies on environmental behaviors of REEs in REE mining areas reviewed above were still limited. We identified some gaps in this research field which need more attention and further improvement.

Firstly, owing to the more active states of REEs in mining areas and their harmful effects on human, a more systematic and in-depth research is needed on the translocation and circulation of REEs in various media in REEs mining areas. The identifications of each transport process of REEs and detailed analysis of their transfer characteristics, such as their forms and the amount of REEs in every single transport pathway, will provide us with a better understanding of the behaviors of REEs in mining areas and a strong base for further health risk assessment of REEs. In addition, with the increasing reports revealing the toxic effects of REEs, the harmful effects of REEs on human health is gradually recognized. People lived in mining areas could be exposed on REEs through different exposure pathways, such as inhalation from air, ingestion from food, drinking waters, and dermal absorption from soils. The high levels of REEs in soils, air, edible parts of plants, and well waters in Chinese REE mining areas are a great threat to human health. The significant

inaccuracy of food REEs detection and the lack of certain standards make it difficult to evaluate health risks of REEs. Therefore, it is necessary to develop guideline values of REEs in foods, drinking waters, and all other environmental components.

Secondly, as we know, high levels of toxic elements in the air have caused serious pollution and threatened human health. The concentrations of organic compounds and heavy metals, such as As, Cu, Pb, and Hg, in the air have received considerable attention in last decades. However, little work has been devoted to REEs in the air. By now, data about concentrations, forms, and distribution characteristics of atmospheric REEs in Chinese REE mining areas are inadequate. Considering the fact that inhalation is the main exposure pathway of REEs for people living around REEs mining areas, more studies focusing on the behavior of REEs in ambient air of REE mining areas in China should be carried out in the future. Furthermore, we suggest more attention to be paid on mining areas with windy conditions and smelting processes, both of which could contribute to further scattering of REES and lead to serious air pollution.

At last, there are numerous methods for pretreatment and detection of REEs when measuring their contents and forms, such as spectrophotometric method, INAA, and NAA in the past decades, and more advanced methods like ICP-MS, ICP-AES, and EXAFS in recent years. However, the accuracy for different methods varies, and the detected number of REEs also varies. We suggest standardized methods on the analysis of REEs in the environment which will enhance the comparability for different researches.

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References

- Aguilar, J., Dorronsoro, C., Fernández, E., Fernández, J., García, I., Martín, F., et al. (2004). Soil pollution by a pyrite mine spill in Spain: evolution in time. *Environmental Pollution*, 132, 395–401.
- Arimoto, R., Duce, R. A., & Ray, B. J. (1989). Concentrations, sources and air-sea exchange of trace elements in the

- atmosphere over the Pacific Ocean. In J. P. Riley & R. Chester (Eds.), *Chemical Oceanography* (Vol. 10, pp. 107–149). San Diego: Academic.
- Braun, J. J., Pagel, M., Muller, J. P., Bilong, P., Michard, A., & Guille, t. B. (1990). Cerium anomalies in lateritic profiles. *Geochimica et Cosmochimica Acta*, 54, 781–795.
- Brown, J. A., Kunz, F. W., & Belitz, R. K. (1991). Characterization of automotive catalysts using inductively coupled plasm mass spectrometry: sample preparations. *Journal of Analytical Atomic Spectrometry*, 6, 393–395.
- Brummer, G. B. (1986). Heavy metal species: mobility and availability in soils. In M. Bernhard, F.E. Brinckman, P.J Sadlers. (Eds.), The importance of chemical “speciation” in environmental progress (pp. 169–192). Berlin: Springer.
- Cao, X. D., Chen, Y., Wang, X. R., & Deng, X. H. (2001). Effects of redox potential and pH value on there lease of rare earth elements from soil. *Chemosphere*, 44, 655–661.
- Castor, B., James, B. H. (2006). Rare earth elements. In E. K. Jessica, C. T. Nikhil, M. B. James (Eds.), *Industrial minerals and rocks*. Society for Mining, Metallurgy and Exploration, 769–792. <http://www.rareelementresources.com/i/pdf/RareEarths-CastorHedrickIMAR7.pdf>.
- Chen, Z. H. (2011). Global rare earth resources and scenarios of future rare earth industry. *Journal of Rare Earths*, 29, 1–6.
- Chen, B. R., Yang, S. J., Yang, Y. N., & Qian, Q. F. (1985). Characteristics of rare-earth elements in the atmospheric particulate in Tianjin. *Environmental chemistry*, 5, 58–62.
- Cheng, J. Z., & Che, L. P. (2010). Current mining situation and potential development of rare earth in China. *Chinese Rare Earths*, 31, 65–69.
- Diatloff, E., Asher, C. J., & Smith, F. W. (1993). Use of Geochem-PC to predict rare earth element (REE) species in nutrient solutions. *Plant and Soil*, 155, 251–256.
- Ding, S. M., Liang, T., Wang, L. J., Zhang, C. S., & Sun, Q. (2005a). Advance in study on dissolved rare earth elements in terrestrial water and their distribution characteristics and basic controlling factors. *Chinese Rare Earths*, 26, 53–61.
- Ding, S. M., Liang, T., Zhang, C. S., Yan, J. C., & Zhang, Z. L. (2005b). Accumulation and fractionation of rare earth elements (REEs) in wheat: controlled by phosphate precipitation, cell wall absorption and solution complexation. *Journal of Experimental Botany*, 56, 2765–2775.
- Ding, S. M., Liang, T., Zhang, C. S., Yan, J. C., Zhang, Z. L., Huang, Z. C., et al. (2007). Fractionations of rare earth elements (REEs) in plants and their conceptive model. *Science in China. Series C, Life Sciences*, 50, 47–55.
- Elderfield, H., Upstill-Goddard, R., & Sholkvitz, E. R. (1990). The rare earth element in rivers, estuaries, and coastal seas and their significance to the composition of oceans waters. *Geochimica et Cosmochimica Acta*, 54, 971–991.
- EPA (2012). Rare earth elements: a review of production, processing, recycling, and associated environmental issues. EPA600/R-12/572.
- Eskenazy, G. M. (1999). Aspects of the geochemistry of rare earth elements in coal: an experimental approach. *International Journal of Coal Geology*, 38, 285–295.
- Feng, F. F., Akagi, T., Yabuki, S., & Iwaki, M. (2001). The variation of REE (rare earth elements) patterns in soil-grown plants: a new proxy for the source of rare earth elements and silicon in plants. *Plant and Soil*, 235, 53–64.
- Feng, F. F., Akagi, T., Yabuki, S., Iwaki, M., & Ogura, N. (2002). Distribution of rare earth elements in seaweed: implication of two different sources of rare earth elements and silicon in seaweed. *Journal of Phycological*, 36, 62–70.
- Feng, L. X., Xiao, H. Q., He, X., Li, Z. J., Li, F. L., Liu, N. Q., et al. (2005). Long-term effects of lanthanum intake on the neurobehavioral development of the rat. *Neurotoxicology and Teratology*, 28, 119–124.
- Gao, X. J., Zhang, S., & Wang, L. J. (2001). Environmental chemistry of rare earth elements (REEs) in the cultivated soil of typical REE mine in the Southern Jiangxi. *Soil and Environmental science*, 10, 11–13.
- Gao, Y. S., Zeng, F. L., Yi, A., Ping, S., & Jing, L. (2003). Research of the entry of rare earth elements Eu^{3+} and La^{3+} into plant cell. *Biological Trace Element Research*, 91, 253–265.
- Garbisu, C., & Alkorta, I. (2001). Phytoextraction: a cost-effective plant based technology for the removal of metals from the environment. *Bioresource Technology*, 77, 229–236.
- Guo, F. Q., Wang, Y. Q., Sun, J. X., & Chen, H. M. (1996). Preliminary study on rare earth bound proteins in natural plant fern *Dicranopteris dichotoma*. *Journal of Nuclear and Radiochemistry*, 18, 133–139.
- Han, F., Shan, X. Q., Zhang, J., Xie, Y. N., Pei, Z. G., Zhang, S. Z., et al. (2005). Organic acids promote the uptake of lanthanum by barley roots. *New Phytologist*, 165, 481–492.
- He, J., Mi, N., Kuang, Y. C., Fan, Q. Y., Wang, X., Guan, W., et al. (2004a). Speciation and distribution characters of rare earth elements in the Baotou section of the Yellow River. *Environmental Science*, 25, 61–66.
- He, J., Mi, N., Kuang, Y. C., Fan, Q. Y., Wang, X., Guan, W., et al. (2004b). Distribution characteristics of LREE in particulates of the Baotou section of the Yellow River. *Acta Sedimentologica Sinica*, 22, 500–506.
- He, J., Mi, N., Kuang, Y. C., Fan, Q. Y., Wang, X., Guan, W., et al. (2004c). Distribution characters of rare earth elements (REEs) in sediment cores from Baotou section of the Yellow River. *Journal of Agro-Environment Science*, 23, 250–254.
- Heinz, K. W., & Robert, E. P. (1993). Acid extractable rare elements in Florida citrus soils and trees. *Communication Soil Science Plant*, 24, 2059–2068.
- Hirano, S., & Suzuki, K. T. (1996). Exposure, metabolism, and toxicity of rare earths and related compounds. *Environmental Health Perspectives*, 104, 85–95.
- Hong, F. S., Wei, Z. G., Tao, Y., Wan, S. K., Yang, Y. T., Cao, X. D., et al. (1999). Distribution of rare earth elements and structure characterization of chlorophyll lanthanum in a natural plant fern *Dicranopteris dichotoma*. *Acta Botanica Sinica*, 41, 851–854.
- Hong, Y., Zhou, D. P., Ma, Y. J., & Liu, N. W. (2010). Trace element concentrations and distribution of atmospheric fine particles in the summer-fall in Shenyang. *China Environmental Science*, 30, 972–979.
- Hu, Q. H., & Jin, M. L. (2000). The chemical behavior and biological effects of rare earth elements in aquatic environment. *Agro-environmental protection*, 19, 274–277.
- Hu, Z. Y., Haneklaus, S., Sparovek, G., & Schnug, E. (2006). Rare earth elements in soils. *Communication Soil Science Plant*, 37, 1381–1420.
- Husain, M. H., Dick, J., & Kaplan, Y. (1980). Rare earth pneumoconiosis. *Occupational Medicine*, 30, 15.

- Ichihashi, H., Morita, H., & Tatsukawa, R. (1992). Rare earth elements (REEs) in naturally grown plants in relation to their variation in soils. *Environmental Pollution*, 76, 157–162.
- Ji, H. B., Wang, L. J., Dong, Y. S., Wang, S. J., Luo, J. M., & Sun, Y. Y. (2004). An overview on the study of biogeochemical cycle for rare earth elements (REEs). *Progress in Geography*, 23, 51–61.
- Jones, D. L. (1997). Trivalent metal (Ce, Y, Rh, La, Pr, Gd) sorption in two acid soils and its consequences for bioremediation. *European Journal of Soil Science*, 48, 697–702.
- Kitto, M. E., Anderson, D. L., Gordon, G. E., & Olmen, I. (1992). Rare earth distributions in catalysts and airborne particles. *Environmental Science and Technology*, 26, 1368–1375.
- Klukanová, A., & Rapant, S. (1999). Impact of mining activities upon the environment of the Slovak Republic: two case studies. *Journal of Geochemical Exploration*, 66, 299–306.
- Li, Q. F., Mao, Z. W., Zhu, Y. X., Huo, D. W., Zhao, H. Z., Yin, X. L., et al. (1992). Studies on the concentration and distribution of REEs in *Dicranopteris dichotoma*. *Chinese Rare Earths*, 13, 16–19.
- Li, Q., Shen, Y. B., & Liu, W. B. (1995). The absorption and distribution of Ce in roots of *Populus deltoides* Lux and their impact to other nutrient elements. *Journal of China Rare Earth Society*, 13, 355–360.
- Li, J. X., Hong, M., & Yin, X. Q. (2008). Accumulation and geochemical characteristics of exogenous rare earths in soil of leeward area of tailings dam of Baotou Iron & Steel (Group) Company. *Chinese Rare Earths*, 29, 57–62.
- Li, Y. X., Zhang, L., & Zhou, X. M. (2010). Resource and environment protected exploitation model for ion-type rare earth deposit in southern of China. *China Rare Earths*, 31, 80–85.
- Liang, T., Ding, S. M., Song, W. C., Chong, Z. Y., Zhang, C. S., & Li, H. T. (2008). A review of fractionations of rare earth elements in plant. *Journal of Rare Earths*, 26, 7–15.
- Liu, J. Y., Chang, X. Y., & Tu, X. L. (2006). Review on heavy metal pollution in mine exploitation. *Mineral Resources and Geology*, 12, 645–650.
- Lu, G. C., Gao, Z. H., Meng, Y. X., Chen, Q., Ren, S. Y., Tang, X. K., et al. (1995). Hygienic investigation of different rare earth (RE) mining areas in China: RE levels of farmer's natural living environment and head hair. *Chinese Journal of Environmental Science*, 4, 78–82.
- Luís, A. T., Teixeira, P., Almeida, S. F. P., Matos, J. X., & Silva, E. F. (2011). Environmental impact of mining activities in the Lousal area (Portugal): chemical and diatom characterization of metal-contaminated stream sediments and surface water of Corona stream. *Science of the Total Environment*, 409, 4312–4325.
- Ma, Y. J., Huo, R. K., Xu, Z. F., Zhang, H., & Liu, C. Q. (2004). REE behavior and influence factors during chemical weathering. *Advances in Earth Science*, 19, 87–94.
- Meng, X. L., & Ji, H. B. (2007). Contents and distribution pattern of dissolved rare earth elements in Ganjiang River in the Southern Jiangxi Province. *Journal of Chinese Rare Earth Society*, 25, 625–637.
- Meng, X. L., & Ji, H. B. (2008). Advance in study on rare earth elements in waters and their geochemistry. *Journal of Capital Normal University(Natural Science Edition)*, 29, 64–68.
- Miekeley, N., Casartelli, E. A., & Dotto, R. M. (1994). Concentration levels of rare-earth elements and thorium in plants from the Morro do Ferro environment as an indicator for the biological availability of transuranium elements. *Journal of Radioanalytical and Nuclear Chemistry*, 182, 75–79.
- Milliman, J. D., & Meade, R. (1983). World-wide deliver of river sediments to the oceans. *Journal of Geology*, 91, 1–21.
- Natarajan, K. A., Subramanian, S., & Braun, J. J. (2006). Environmental impact of metal mining- biotechnological aspects of water pollution and remediation—an Indian experience. *Journal of Geochemical Exploration*, 88, 45–48.
- Chinese Ministry of Health (2005). Maximum levels of contaminants in foods GB2762-2005, Beijing, China.
- Olmez, L., & Gordon, G. E. (1985). Reports: rare earths: atmospheric signatures for oil-fired power plants and refineries. *Science*, 229, 966–968.
- Peng, A., & Wang, Z. J. (1995). Recent research progress on environmental chemistry of rare earth elements. *Advances in Environmental Science*, 3, 22–32.
- Protano, G., & Riccobono, F. (2002). High contents of rare earth elements (REEs) in stream waters of a Cu–Pb–Zn mining area. *Environmental Pollution*, 117, 499–514.
- Quiquampoix, H., Ratcliffe, R. G., Ratkovic, S., & Vucinic, Z. (1990). ¹H and ³¹P NMR investigation of gadolinium uptake in maize roots. *Journal of Inorganic Biochemistry*, 38, 265–275.
- Ran, Y., & Liu, Z. (1992). Characteristics of adsorption and desorption of REEs on main type soils of China. *Journal of Chinese Rare Earth Society*, 10, 377–380.
- Robert, H. B., Liu, X. W., & Schijf, J. (1996). The influence of phosphate coprecipitation on rare earth distributions in natural waters. *Geochimica et Cosmochimica Acta*, 60, 3341–3346.
- Robinson, W. O. (1943). The occurrence of rare earths in plants and soils. *Soil Science*, 56, 1.
- Salomons, W. (1995). Environmental impact of metals derived from mining activities: processes, predictions, prevention. *Journal of Geochemical Exploration*, 52, 5–23.
- Shan, X. Q., Wang, H. I., Zhang, S. Z., Zhou, H. F., Zheng, Y., Yu, H., et al. (2003). Accumulation and uptake of light rare earth elements in a hyperaccumulator *Dicranopteris dichotoma*. *Plant Science*, 165, 1343–1353.
- Sholkovitz, E. D. (1994a). Ocean particle chemistry: the fractionation of rare earth elements between suspended particles and seawater. *Geochimica et Cosmochimica Acta*, 58, 1567–1579.
- Sholkovitz, E. R. (1994b). The aquatic chemistry of rare earth elements in rivers and estuaries. *Aquatic Geochemistry*, 1, 1–34.
- Sholkovitz, E. D., Church, T. M., & Arimoto, R. (1993). Rare earth element composition of precipitation, precipitation particles, and aerosols. *Journal of Geophysical Research*, 98, 20587–20599.
- Sholkvitz, E. R. (1993). The geochemistry of rare earth element in the Amazon River estuary. *Geochimica et Cosmochimica Acta*, 57, 2181–2190.
- Sholkvitz, E. R. (1995). The aquatic chemistry of rare earth element in rivers and estuaries. *Aquatic Geochemistry*, 1, 1–34.
- Sugimae, A. (1980). Atmospheric concentrations and sources of rare earth elements in the Osaka area. *Japan Atmospheric Environment*, 14, 1171–1175.

- Sultan, K., & Shazili, N. A. (2009). Rare earth elements in tropical surface water, soil and sediments of the Terengganu River Basin. *Malaysia Journal of Rare Earths*, 27, 1073–1078.
- Suzuki, Y., Hikida, S., & Furuta, N. (2011). Cycling of rare earth elements in the atmosphere in central Tokyo. *Journal of Environmental Monitoring*, 13, 3420–3428.
- Tagami, K., & Uchida, S. (2005). Transfer of REEs from nutrient solution to radish through fine roots and their distribution in the plant. *Journal of Alloys and Compound*, 408, 409–412.
- Taylor, S. R., & McLennan, S. M. (1985). *The continental crust its composition and evolution* (p. 311). Oxford: Blackwell.
- Teng, Y. G., Ni, S. J., Jiao, P. C., Deng, J., Zhang, C. J., & Wang, J. S. (2004). Eco-environmental geochemistry of heavy metal pollution in Dexing mining area. *Chinese Journal of Geochemistry*, 23, 349–358.
- Anonymous, 2012. Situation and Policy of China's Rare Earth Industry, White Paper (English Version). The State Council Information Office of the People's Republic of China <http://www.scio.gov.cn/zfbps/ndhf/2012/Document/1175419/1175419.htm>.
- Thomas, W. A. (1975). Accumulation of rare earths and circulation of cerium by mockernut hickory trees. *Canadian Journal of Botany*, 53, 1159–1165.
- Tyler, G. (2004). Rare earth elements in soil and plant systems—a review. *Plant soil*, 267, 191–206.
- Volokh, A. A., Gorbunov, A. V., Gundorina, S. F., Revich, B. A., Frontasyeva, M. V., & Palvolokh, C. S. (1990). Phosphorus fertilizer production as a source of rare-earth elements pollution of the environment. *Science of the Total Environment*, 95, 141–148.
- Wang, Z. W. (2003). *Rare earth elements of atmosphere and effects of rare earth elements on emission of green house gases*. Master Dissertation: Guangxi University.
- Wang, L. F. (2005). Studies on the photosynthetic characterizations and distributions of rare earth elements in fern *Dicranopteris dichotoma*. PH.D Dissertation, Institute of Botany, Chinese Academy of Science.
- Wang, Z. G., Yu, X. Y., & Zhao, Z. H. (1989). *The geochemistry of rare earth elements* (p. 321). Beijing: Science Press.
- Wang, L. J., Zhang, S., & Zhang, C. S. (1995). Aquatic environmental geochemistry characteristics of rare earth elements in the middle-lower reaches of Changjiang (Yangtze) river. *Acta Scientiae Circumstantiae*, 15, 57–65.
- Wang, Y. Q., Sun, J. X., Chen, H. M., & Guo, F. Q. (1997). Study on contents and distribution characteristics of rare earths in natural plants by NAA. *Journal of Chinese Rare Earth Society*, 15, 160–164.
- Wang, L. J., Zhang, C. S., Zhang, S., Chen, N., & Yang, L. (1998). Geochemical characteristics of rare earth elements in the Zhujiang River in Guangzhou. *Acta Geographical Sinica*, 53, 453–462.
- Wang, C. X., Zhu, W., Wang, Z. J., & Guicherit, R. (2000a). Rare earth elements and other metals in atmospheric particulate matter in the western part of the Netherlands. *Water Air Soil Pollution*, 121, 109–118.
- Wang, Z. L., Liu, C. Q., Xu, Z. F., Zhu, J. M., & Zhang, J. (2000b). Advances in research on geochemistry of rare earth elements in rivers. *Advance in Earth Sciences*, 15, 553–558.
- Wang, C. X., Zhu, W., Wang, Z. J., Peng, A., & Guicherit, R. (2001a). Comparative studies on the concentration of rare earth elements and heavymetals in the atmospheric particulate matter in Beijing, China, and in Delft, the Netherlands. *Environmental International*, 26, 309–313.
- Wang, Y. Q., Sun, J. X., Zhang, Z. Y., Guo, F. Q., Chen, H. M., & Jiang, P. (2001b). Study on REEs speciation in natural plant by MAA. *Nuclear Techniques*, 24, 721–726.
- Wang, L. J., Liang, T., Hu, A. T., Ding, S. M., Zhang, C. S., & Yan, X. (2005). Accumulation and fractionation of rare earth elements in soil–rice system. *Journal of Rare Earths*, 23, 747–751.
- Wang, L. F., Ji, H. B., & Tian, W. M. (2010). Fine location of rare earths and effects of light inhibition on photosynthetic characterization of *D. dichotoma* in a heavy rare earth mine. *Journal of Chinese Rare Earth Society*, 28, 379–386.
- Wei, F. S., Zheng, C. J., Chen, J. S., & Wu, Y. Y. (1991). Study on the background contents on 61 elements of soils in China. *Chinese Journal of Environmental Science*, 12, 12–20.
- Wei, Z. H., Hong, F. S., Zhao, G. W., Tao, Y., Hu, T. D., Liu, T., et al. (2000). Determination of double decker sandwich structured La-substituted chlorophyll *a* by EXAFS. *Acta Chimica Sinica*, 58, 559–562.
- Wei, Z. G., Yin, M., Zhang, X., Hong, F. S., Li, B., Tao, Y., et al. (2001). Rare earth elements in naturally grown fern *Dicranopteris linearis* in relation to their variation in soils in South Jiangxi region (Southern China). *Environmental Pollution*, 114, 345–355.
- Wei, Z. G., Zhang, H. J., Li, H. X., & Hu, F. (2006). Research trends on rare earth element hyperaccumulator. *Journal of Chinese Rare Earth Society*, 24, 1–11.
- Wytenbach, A., Furrer, V., Schleppe, P., & Tobler, L. (1998). Rare earth elements in soil and in soil-grown plants. *Plant and Soil*, 199, 267–271.
- Xiao, H. Q., Zhang, Z. Y., Li, F. L., & Chai, Z. F. (2003). Study on contents and distribution characteristics of REE in fern by NAA. *Nuclear Techniques*, 26, 420–424.
- Xu, X. K. (2005). Research advances in the behavior and fate of rare earth elements in soil–plant systems. *Journal of Agro-environmental Science*, 24, 315–319.
- Yang, Y. G. (1996). Agricultural geochemical studies of the rare earth elements. *Earth and Environmental*, 24, 39–43.
- Yang, S. J., Yang, Y. N., Chen, B. R., & Chen, B. (1993). Characterization of marine aerosol and its sources over the western Pacific ocean. *Acta Scientiae Circumstantiae*, 13, 135–142.
- Yu, J., Huang, Z. Y., & Chen, T. (2009). Determination of rare-earth elements (REEs) in orange-growing soils and navel oranges around rare-earth mining area in southern Jiangxi. *Food Science*, 30, 309–313.
- Zhang, L. C., Zhang, S., Dong, W. J., & Wang, L. J. (1992). *The geochemical research of water environment in the source regions of Changjiang River* (pp. 61–199). Beijing: China Environmental Science Press.
- Zhang, H., Liu, Y. H., & Ma, Y. F. (1997). Simultaneous determination of rare earth in rare earth ore band tea-leaves by ICP-AES. *Spectroscopy Spectrom Analytical*, 17, 74–78.
- Zhang, H., Feng, J., & Zhu, W. F. (1999). Characteristic of rare earth distribution in biologic chains of rare earth rich background regions. *Journal of Chinese Rare Earth Society*, 17, 365–368.

- Zhang, Z. Y., Wang, Y. Q., Sun, J. X., & Li, F. L. (2000a). Chemical species of rare earth elements in RE hyperaccumulator *Dicranopteris dichotoma*. *Chinese Rare Earths*, 21, 42–45.
- Zhang, Z. Y., Wang, Y. Q., Sun, J. X., Li, F. L., Chai, Z. F., Xu, L., et al. (2000b). Determination of rare earth elements in plant protoplasts by MAA. *Chinese Science Bulletin*, 45, 1497–1499.
- Zhang, Z. Y., Wang, Y. Q., Li, F. L., Zhao, H. Q., & Chai, Z. F. (2002). Distribution characteristics of rare earth elements in plants from a rare earth ore area. *Journal of Radioanalytical and Nuclear Chemistry*, 252, 461–465.
- Zhang, Q. H., Tong, L. G., Cheng, L., Zhu, J., & Wang, Q. (2012). Characteristics of REE distribution in the surface soil of the farmland in wastewater irrigation area. *Acta Agriculturae Universitatis Jiangxiensis.*, 34, 0614–0618.
- Zhou, G. H., Sun, B. B., Liu, Z. Y., Wei, H. L., Zeng, D. M., & Zhang, B. M. (2012). Geochemical feature of rare earth elements in major rivers of eastern China. *Geoscience*, 26, 1028–1042.
- Zhu, J. G., Xing, G. X., Yamasaki, S., & Tsumura, A. (1993). Adsorption and desorption of exogenous rare earth elements in soils: I. Rate of forms of rare earth elements sorbed. *Pedosphere*, 3, 299–308.
- Zhu, W. M., Zhang, J. Z., & Zhang, L. G. (1996). Numericals imulation of RE migration in soils. *Journal of Chinese Rare Earth Society*, 14, 341–346.
- Zhu, W. F., Xu, S. Q., Shao, P. P., Zhang, H., Feng, J., Wu, D. L., et al. (1997). Investigation on intake allowance of rare earth-A study on bio-effect of rare earth in South Jiangxi. *China Environmental Science*, 17, 63–66.
- Zhu, J. H., Yuan, Z. K., Wang, X. Y., & Yan, S. M. (2002). Investigation on the contents of rare earth elements in environment of rare earth ore area in Jiangxi. *Environmental Health*, 19, 443–448.
- Zhu, J. H., Yuan, Z. K., Pan, X. C., & Yan, S. M. (2003). Determination on rare earth level in air. *Chinese Journal of Public Health*, 19, 1414–1415.