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Distribution of rare earth elements in PM_{10} emitted from burning coals and soil-mixed coal briquettes

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ABSTRACT

Emission from burning coals is one of the major sources of the airborne particles in China. We carried out a study on the rare earth elements (REEs) in the inhalable particulate matter (PM_{10}) emitted from burning coals and soil-coal honeycomb briquettes with different volatile contents and ash yields in a combustion-dilution system. Gravimetric analysis indicates that the equivalent mass concentration of the PM_{10} emitted from burning the coals is higher than that emitted from burning the briquettes. The ICP-MS analysis indicates that the contents of total REEs in the coal-burning PM_{10} are lower than those in the briquette-burning PM_{10}. In addition, the contents of the light rare earth elements (LREEs) are higher than those of the heavy rare earth elements (HREEs) in the PM_{10} emitted from burning the coals and briquettes, demonstrating that the REEs in both the coal-burning and briquette-burning PM_{10} are dominated by LREEs. The higher contents of total REEs and LREEs in the coal-burning PM_{10} are associated with the higher ash yields and lower volatile contents in the raw coals. A comparative analysis indicates that the La/Sm ratios in the PM_{10} emitted from burning the coals and briquettes, being lower than 2, are lower than those in the particles from gasoline-powered vehicle emission.

Introduction

In recent years, haze has become increasingly frequent during the spring and winter in northern China. Emission from fossil fuel combustion is believed to be the major sources of the haze particles (Bi et al., 2007; Xie et al., 2008; Wei et al., 2018). China is the largest coal producer and consumer in the world. In China, coal production accounted for 69.3% of total energy production and coal consumption accounted for 59% of total energy consumption in 2018 (China Statistic Department, 2019). The coal-burning emission represents an important source of gaseous and particulate pollutants in the ambient air of the heavily populated Beijing-Tianjin-Hebei area of northern China (Cai et al., 2018). Coal contains many potentially harmful substances (Shao et al., 2015; Finkelman and Tian, 2017). The particulate pollutants emitted from burning coals can have a significant impact on atmospheric chemistry, climate change, and human health (Jones et al., 2009; Kan et al., 2012; Pian et al., 2016; Shao et al., 2016). In addition, residential coal-burning stoves are commonly used for cooking and heating, especially in the spring and winter. It has been argued that the haze

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in northern China is closely related to coal-burning emissions from domestic heating and cooking (Li et al., 2012). It is suggested that the focus of Chinese $PM_{2.5}$ pollution control policy should be on controlling overall coal consumption and the treatment of scattered coal consumption should be the top priority (Xie et al., 2020).

To date, more and more studies of atmospheric environments have been focused on the physicochemical characteristics of individual aerosol particles (Niu et al., 2016a and 2016b; Xing et al., 2017; Shao et al., 2017), the source of atmospheric particles (Polidori et al., 2010; Ambade, 2014), the chemical composition of atmospheric aerosol (Ji et al., 2016), the characteristics of volatile organic compounds (VOCs) (Vo et al., 2018), and the oxidative potential of atmospheric particles (Shao et al., 2013; Xiao et al., 2014). It has been noticed that many toxic and harmful heavy metals were associated with the particulate matters emitted from coal combustion (Lu et al., 2009; Ambade, 2014; Tao et al., 2014; Zhai et al., 2014; Chen et al., 2015; Song et al., 2015; Hou et al., 2016; Liu et al., 2016; Censi et al., 2017; Finkelman et al., 2018). Some studies have focused on the distribution of REEs in atmospheric particulate matter (Wang et al., 2012; Wang et al., 2014a; Wang et al., 2014b; Zhang et al., 2014; Dai et al., 2016). The La/Sm ratio was identified as an indicator of different emission sources (Kitto et al., 1992). However, few studies dealt with the distribution of REEs in coal-burning emissions. So far, no consensus has been achieved for quantifying the components released by coal burning, thus leading to diversified results in the source apportionment of atmospheric particulate matter (Lu et al., 2009; Zhu et al., 2012; Huang et al., 2014).

We studied the REEs in PM_{10} emitted from a coal-burning process by using a combustion-dilution system in a laboratory and an Inductively Coupled Plasma Mass Spectrometer (ICP-MS). The results not only can provide a scientific reference and the corresponding data support for the source apportionment of atmospheric particles, but can also potentially provide important insights that may result in effective control of inhalable particulate matter emitted from coal-burning processes.

1. Sampling and experiments

1.1. Sample collection

1.1.1. Inhalable particle collection from coal-burning emission source

The raw coals and soil-coal honeycomb briquettes used in this study were prepared from the samples collected from a number of coal mining areas, including Dongsheng in the Inner Mongolia Autonomous Region (DS), Zhijin in Guizhou Province (ZJ), Datong in Shanxi Province (DT), Jingxi (western Beijing) in Beijing (JX), and Yinchuan in the Ningxia Hui Autonomous Region (YC). The soil-coal honeycomb briquettes were prepared from DS, ZJ and DT coals by a combination of 80% raw powdered coals and 20% soil. Due to different sedimentary environments and geologic histories, the ash yields and the volatile contents in raw coals from different areas are different. The raw coals from DS, DT and ZJ are low ash-yield coal, in which the DS and DT coals are high volatile coal, but the ZJ coal is a low volatile coal. In addition, the JX and YC coals are high ash-yield coals, in which the JX coal is a low-volatile coal, but the YC coal a higher-volatile coal. Information about the proximate analysis of the raw coals used in this study is given in Table 1.

The coal-burning experiment was conducted in a combustion-dilution system that is based at the Laboratory of the Chinese Research Academy of Environmental Sciences. The system was composed of a combustion stove with smoke dilution tunnels and smoke chambers (Geng et al., 2012). The smoke chamber was connected to the horizontal cylindrical tunnel that was used for real-time measurement of gaseous and particulate pollutants during the combustion experiments. Our PM_{10} sampler was connected to this smoke chamber. During the experiments, the flow rate of the diluted flue gas into smoke chamber was fixed at 100 L/min. The detailed information about the combustion-dilution system used in this study was given in Shao et al. (2016).

A medium-volume particle sampler (Dickel-80, Beijing Geological Instrument Dickel Cooperation Limited, China) connected to the dynamic smoke chamber, was used to collect the particulate matter. Particles with an aerodynamic diameter of 10 μm or lower (PM_{10}) were collected. Quartz fiber filters (diameter 90 mm) were used in the Dickel-80 sampler (flow rate 78 L/min).

Table 1 – Proximate analysis of the raw coals used in this study.

Raw coal (C)	M_{ad} (%)	A_{ad} (%)	V_{ad} (%)	FC_{ad} (%)
DS-C	7.46	6.68	30.82	55.04
DT-C	6.98	9.5	32.07	51.45
ZJ-C	0.94	9.08	5.76	84.22
JX-C	3.02	26.34	4.44	66.2
YC-C	1.3	23.28	19.74	55.68

M_{ad}: moisture contents; A_{ad}: ash yields; V_{ad}: volatile contents; FC_{ad}: fixed carbon content; ad: air dry base.
DS: Dongsheng in the Inner Mongolia Autonomous Region, ZJ: Zhijin in Guizhou Province, DT: Datong in Shanxi Province; JX: Jingxi (western Beijing) in Beijing; YC: Yinchuan in the Ningxia Hui Autonomous Region. The DS, DT and YC coals belong to Jurassic, the ZJ coal belongs to Late Permian, the JX coals belong to Carboniferous-Permian for the geological ages

1.2. Sample pretreatment and experimental method

1.2.1. Sample pretreatment

The sample-loaded filters, together with two blank filters, were incubated in HPLC-grade water. The incubations were gently agitated in a vortex mixer (Scientific Industries, Vortex Genie 2, USA) for 20 hr at room temperature to ensure the maximum mixing of the sample in the water and to avoid sedimentation. After incubation each sample was separated into two parts; one part was taken to represent the whole-particle suspension, and another part was preserved to prepare the water-soluble fraction for future bioreactivity study. The whole-particle suspensions were used for the REE measurements in this study.

1.2.2. Experimental method

This study used a high-resolution Inductively Coupled Plasma Mass Spectrometer (ICP-MS, model number: ELEMENT; Manufacturer: Finnigan-MAT company) for the analysis of REEs with a detection limit from 1 ppt to 1 ppb (10^{-12}–10^{-9}). The experiments were carried out at a laboratory in the Beijing Research Institute of Uranium Geology. The whole-particle suspensions were digested with high purity nitric acid, hydrofluoric acid (1.5 mL), nitric acid (0.5 mL) and perchloric acid (0.5 mL). Digestions were carried out in a CEM MDS-200 microwave system, using CEM advanced composite vessels with Teflon liners. The digested samples were then concentrated by evaporating the nitric acid and by re-dissolving in 2 mL of 10% nitric acid. Samples were diluted to a 20 mL volume using demonized (>18 MU) water. One milliliter of each sample was combined with a 50 ppb thallium standard (1 mL) and this solution was made up to 10 mL with 2% nitric acid to be analyzed in the ICP-MS. In this study, rare earth elements La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu were measured. The final results were reported as the ppm (μg/g) of each element in the intact PM_{10}.

2. Results

2.1. Equivalent mass concentrations of PM_{10} emitted from burning coals and briquettes

In this study, the coals and briquettes were combusted to investigate the equivalent mass concentration of PM_{10} emitted from burning the coals and briquettes. The same amount of coals and briquettes, time of combustion, combustion conditions, combustion-dilution system, sampler and filter were used in the experiment for all coals and briquettes. The mass concentration can be calculated

Table 2 – Equivalent mass concentrations of PM_{10} emitted from burning coals (C) and briquettes (B).

Raw coal (C) and briquette (B)	Mass (μg)	Sampling time (min)	Flow rate (L/min)	Mass concentration ($\mu g/m^3$)
DS-B	3400	56	78	778.4
DS-C	29,500	41	78	9224.5
ZJ-B	7800	78	78	1282.1
ZJ-C	12,400	60	78	2649.6
DT-B	4300	80	78	689.1
DT-C	18,100	54	78	4297.2
JX-C	4900	50	78	1256.4
YC-C	8700	29	78	3846.2

by following formula:

$$MC = (M_2 - M_1)/V$$

where, MC ($\mu g/m^3$) represents the equivalent mass concentration of PM_{10} emitted from burning the coals and briquettes; M_1 (μg) represents the mass of the filters before sampling; M_2 (μg) represents the mass of the filters after sampling; V (m^3) represents the sampling volume, which is the value of sampling time multiplied by the flow rate of the sampler.

Table 2 shows the equivalent mass concentration of PM_{10} emitted from burning the coals and briquettes. The mass concentrations of the coal-burning PM_{10} range from 1260 to 9220 $\mu g/m^3$, being generally higher than 1000 $\mu g/m^3$. The mass concentrations of PM_{10} emitted from burning the DS and DT briquettes are lower than 1000 $\mu g/m^3$ (780 and 690 $\mu g/m^3$, respectively), except for the 1280 $\mu g/m^3$ for the ZJ briquettes. It is apparent that the equivalent mass concentration of the coal-burning PM_{10} was higher than that in the briquette-burning PM_{10}.

2.2. *REEs in the PM_{10} emitted from burning coals and briquettes*

2.2.1. *Total REEs in the PM_{10} emitted from burning coals and briquettes*

The contents of REEs in the bulk PM_{10} samples were determined by analyzing the digested whole-particle suspensions, and the water-soluble fraction. Table 3 shows the contents of total REEs in the PM_{10} emitted from burning coals and briquettes samples. It can be seen that the content of total REEs in the PM_{10} emitted from burning JX coals (3.6 ppm) is highest, followed by the PM_{10} emitted from burning ZJ, YC, DT, and DS coals in descending order (2.5, 2.3, 1.9, 1.3 ppm, respectively). Table 3 also showed that the contents of total REEs in the PM_{10} emitted by burning coals and briquettes are different. The contents of the total REEs in the coal-burning PM_{10} range from 1.3 to 3.6 ppm, all less than 4 ppm. The contents of total REEs in the PM_{10} emitted by burning DS, ZJ and DT briquettes are 32.4, 7.6 and 17.8 ppm, respectively, all greater than 7 ppm and higher than those of the coal-burning PM_{10}.

The average value of the REE in the PM_{10} from the 3 samples of burning briquettes and the average value of the REE in the PM_{10} from the 5 samples of burning coals were obtained and are plotted in Fig. 1. It is shown that the content of Ce was highest, followed by Nd, La, Sm, Pr, Lu, Dy, Ho, Eu, Er, Tm, Yb, Gd and Tb in descending order in the coal-burning PM_{10}. However, Ce, La, Nd, Sm, Lu, Dy, Pr, Er, Eu, Tm, Ho, Gd, Yb and Tb are in descending order in the briquette-burning PM_{10}. It is seen that the contents of La, Ce, Nd and Sm in the coal-burning PM_{10} are from 0.3 to 1 ppm, and the total content of these elements accounts for 80% of the REEs. However, the contents of La, Ce, Nd and Sm in the briquette-burning PM_{10} are higher than 2 ppm, and the total contents of these elements account for 75% of the REEs. It is obvious that the content of individual REE in the coal-burning PM_{10} is lower than that in the briquette-burning PM_{10}.

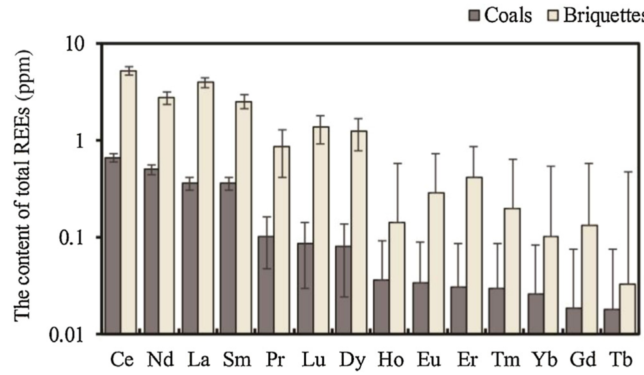

Fig. 1 – Contents of REEs in the PM_{10} emitted from burning coals and briquettes.

2.2.2. *Contents of LREEs and HREEs in PM_{10} emitted from burning coals and briquettes*

The content of LREEs and HREEs are commonly used to characterize the distribution of REEs. In Table 3, the contents of LREEs in the PM_{10} emitted by burning the DS, ZJ, DT, JX and YC coals are 0.8, 2.2, 1.8, 3.2 and 2.01 ppm, respectively. However, the contents of LREEs in the PM_{10} emitted by burning the DS, ZJ and DT briquettes are 25.6, 6.5, 14.7 ppm, respectively. It is apparent that the contents of LREEs in the PM_{10} emitted from burning the coals are lower than those from burning the briquettes. The contents of HREEs in the PM_{10} emitted by burning the coals range from 0.14 to 0.55 ppm, but those from burning the briquettes range from 1.0 to 6.8 ppm. This shows that the contents of HREEs in the PM_{10} emitted from burning the coals are lower than those from burning the briquettes. In addition, the contents of LREEs are higher than those of HREEs in both cases. The same conclusions were obtained from the atmospheric PM_{10} in Wang et al. (2012) and Wang et al. (2014b).

The LREEs/HREEs ratio is used to measure the fractionation between LREEs and HREEs. The LREEs/HREEs ratios are given in Table 3. The LREEs/HREEs ratios from burning the coals range from 3.8 to 13.4, except for the DS coals with a ratio of 1.4. This indicates that the REEs in PM_{10} emitted from burning the coals and briquettes are dominated by LREEs. The similar conclusion was also obtained by a study of the REEs in atmospheric particulate matter of coal-burning heating period in Beijing (Wang et al., 2001).

The REE compositions of the coal-burning PM_{10} are closely related to the REE compositions in the raw coals. Our study has indicated that the REEs in PM_{10} emitted from burning the coals and briquettes are both dominated by LREEs. The contents of LREEs accounted for 79% to 93% of the total REEs in the PM_{10} emitted from burning coals and briquettes, except for 58% in the DS coals. Table 4 shows the average values for LREEs and HREEs from selected coal samples from different geological backgrounds. It can be seen that the REEs in raw coals are dominated by LREEs, and the LREEs account for about 80% to 94% of total REEs. Our results show that the distribution of REEs in the PM_{10} emitted from burning coals is similar to the distribution of REEs in the raw coals, and the LREEs are predominated in both cases. Finkelman et. al (2018) have studied the REEs in coals by sequential leaching experiments, and have also found that the leachates have a higher proportion of LREEs than HREEs.

2.3. *La/Sm ratios in the PM_{10} emitted from burning coals and briquettes*

The La/Sm ratio has been used as the indicator of different emission sources (Kitto et al., 1992). The La/Sm ratios in the REEs from coal-burning emission in this study are compared. The La/Sm ratios in the coal-burning PM_{10} are from 0.55 to 1.96, averaged 1.43. The La/Sm ratios in the PM_{10} emitted by burning DS, ZJ and DT coals are 1.59, 1.86

Table 3 – Contents of total and individual REEs in the PM_{10} emitted from burning coals (C) and briquettes (B) (ppm).

Sample types	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho
DS-B	7.53	6.48	1.54	4.97	4.44	0.64	–	–	2.71	0.20
DS-C	0.16	0.26	0.06	0.19	0.10	–	0.07	0.01	0.03	0.03
ZJ-B	1.38	2.85	0.29	1.21	0.72	0.09	0.08	0.03	0.47	0.06
ZJ-C	0.54	0.92	0.15	0.27	0.29	0.05	–	0.02	0.12	–
DT-B	2.96	6.34	0.73	2.12	2.43	0.12	0.32	0.07	0.49	0.17
DT-C	0.39	0.66	0.08	0.49	0.20	0.01	–	0.01	0.07	0.01
JX-C	0.39	1.04	0.11	0.89	0.71	0.09	0.03	0.03	0.06	0.09
YC-C	0.33	0.46	0.12	0.65	0.50	0.01	–	0.01	0.13	0.05

Sample types	Er	Tm	Yb	Lu	LREEs	HREEs	REEs	LREEs/HREEs
DS-B	0.84	0.47	–	2.55	25.60	6.76	32.36	3.79
DS-C	0.02	0.01	0.04	0.36	0.78	0.55	1.33	1.41
ZJ-B	0.03	0.07	0.10	0.17	6.55	1.02	7.57	6.41
ZJ-C	0.03	0.04	0.05	0.05	2.21	0.30	2.51	7.48
DT-B	0.37	0.07	0.20	1.40	14.70	3.08	17.78	4.77
DT-C	0.02	0.01	0.01	–	1.82	0.14	1.95	13.36
JX-C	0.06	0.07	0.03	0.03	3.24	0.41	3.64	7.91
YC-C	0.03	0.03	–	–	2.07	0.25	2.32	8.25

Note: "–" represents below detection limit.

Table 4 – Contents of REEs in the raw coals from other studies (ppm).

Coal mine	Geologic age	LREEs	HREEs	Total REEs	LREEs/REEs	Data sources
Huangshi, Hubei	Late Permian	126	10	136	0.93	Du and Zhuang, 2006
Chongqing	Late Permian	189	12	201	0.94	
Leping, Jiangxi	Late Permian	68	7	75	0.91	
Liupanshui, Guizhou	Late Permian	91	9	100	0.91	
Panzhihua, Sichuan	Late Triassic	111.01	12.75	123.75	0.90	Chen, 2017
Panzhihua, Sichuan	Late Triassic	144.24	16.63	160.87	0.90	
Nantong, Chongqing	Late Permian	228.19	27.96	256.14	0.89	
Donglin, Chongqing	Late Permian	238.85	23.77	262.61	0.91	
Western Ordos Basin in Ningxia and Gansu	Carboniferous-Permian	142.78	35.732	177.83	0.80	Qin et al., 2016
Western Ordos Basin in Ningxia and Gansu	Middle Jurassic	51.608	12.905	64.513	0.80	

and 1.96, respectively. However, the La/Sm ratios in the PM_{10} emitted by burning JX and YC coals are 0.55 and 0.67, respectively. In any case, all samples have a La/Sm ratio lower than 2.

The La/Sm ratios in the PM_{10} emitted by burning briquettes DS-B and ZJ-B are 1.70 and 1.86, and they are higher than those by burning their corresponding raw coals. The value for the PM_{10} emitted by burning DT-B is 1.22 which is slightly lower than that by burning its corresponding raw coal.

3. Discussion

3.1. *Influence of the raw coal compositions on the mass concentration and the REE compositions of the coal-burning PM_{10}*

3.1.1. *Influence of the raw coal compositions on the mass concentration of PM_{10}*

In order to show the influence of the raw coal compositions on the mass concentration of the PM_{10} emitted from burning these coals, the relationship between the PM_{10} mass concentration and ash yields, volatile contents in the raw coals were investigated. It can be seen from Fig. 2 that the equivalent mass concentration of the PM_{10} emitted from burning DS coal (9225 $\mu g/m^3$) is highest, followed by the PM_{10}s from burning DT, YC, ZJ and JX coals in descending order (4297, 3846, 2650, 1256 $\mu g/m^3$, respectively). It is also showed that the ash yields in raw coals don't have similar variation trends with the equivalent PM_{10} mass

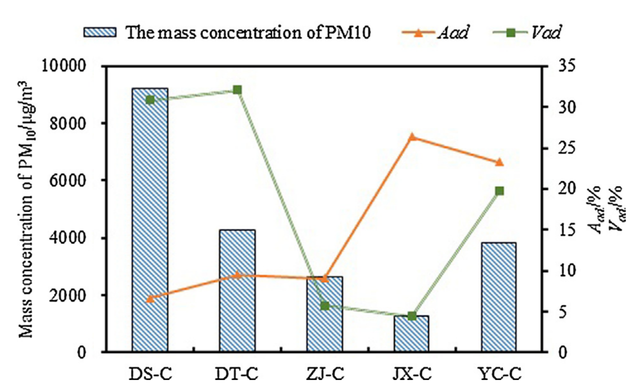

Fig. 2 – The relationship between the mass concentration of the coal-burning PM_{10} and moisture contents, ash yields, volatile contents in the raw coals. Note: "M_{ad}" is moisture content, "A_{ad}" is ash yield, "V_{ad}" is volatile content, "ad" represents air dry base.

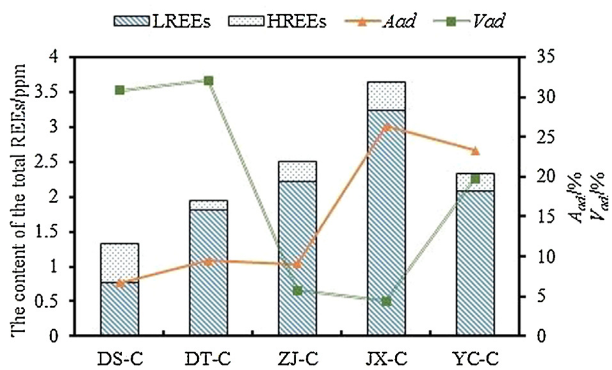

Fig. 3 – The relationship between the contents of REEs in the coal-burning PM_{10} (C) and ash yields, volatile contents in the raw coals. Note: A_{ad} is ash yields, V_{ad} is volatile contents, ad represents air dry base.

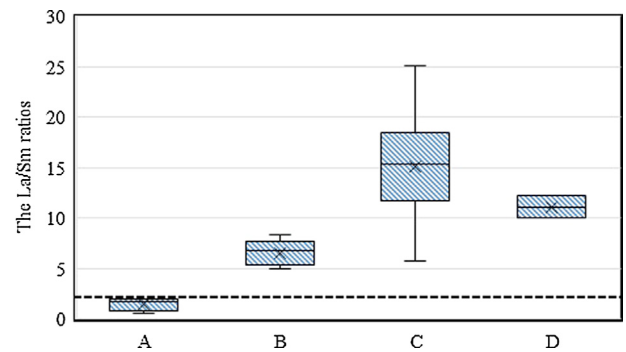

Fig. 4 – Box-plot showing comparison of the La/Sm ratios in particulate matter from different sources. Note: A represents the emission of laboratory coal-burning system in this study, B represents the ambient indoor coal-burning environment (Hu, 2016), C represents the tunnel environment dominated by gasoline vehicle emission (Hou, 2017), D represents the gasoline-powered vehicles emissions by engine test bench (Xing, 2018).

concentration, and the higher ash yields such as the JX coal tends to be associated with the low PM_{10} mass concentrations. In contrast, the volatile contents in raw coals have a clear variation trend with the equivalent PM_{10} mass concentrations, and the higher volatile contents in the DS, DT, and YC coals tend to be associated with the higher PM_{10} mass concentrations. These results suggest that the mass concentration of the coal-burning PM_{10} is mainly related to the volatile contents in the raw coals. As the volatile content is the indicator of the coal ranks with the higher volatile content representing a low coal rank, it can be concluded that the combustion of the high volatile and thus low rank coals could contribute a high PM_{10} concentration.

3.1.2. *Influence of the raw coal compositions on the contents of total REEs in the coal-burning PM_{10}*

The variation trends of the contents of total REEs in the coal-burning PM_{10} with the ash yields, and volatile contents in the raw coals are given in Fig. 3. Overall, the contents of total REEs in the coal-burning PM_{10} are positively correlated with the ash yields, and negatively correlated with the volatile contents in the raw coals, indicating that the REEs in the coal-burning PM_{10} are mainly associated with the ash yields in raw coals. It is noticed that the higher contents of total REEs in the PM_{10} emitted from burning JX and YC coals are attributed to the higher ash yields in coals, and the lower contents of total REEs in the PM_{10} emitted from burning DS and DT coals are due to the lower ash yields in coals. Both the contents of total REEs and LREEs in the coal-burning PM_{10} show similar relationships with the ash yields in coals, but opposite relationships with the volatile contents in the coals. However, there is no significant correlation between the contents of HREEs in the coal-burning PM_{10} and the ash yields, volatile contents in the raw coals.

Some studies showed that there was a close correlation between the contents of total REEs and LREEs in the coals and the ash yields, and there was no significant correlation between the content of HREEs in the coals and the ash yields. In other words, with the increase of ash yields in the coals, the contents of total REEs and LREEs will also increase (Du and Zhuang, 2006; Chen, 2017). The REEs were found to be enriched in fly ashes (Dai et al., 2014). Therefore, the higher ash yields in the coals would result in a higher content of total REEs and LREEs in the coal-burning PM_{10}.

3.2. *Comparisons of the La/Sm ratios in the particulate matter from this study and other studies*

The La/Sm ratio in the particulate matter displays different values in different atmospheric environments and is of potential implication in the source apportionment of airborne particles. Olmez et al. (1985) has demonstrated that the La/Sm ratios for atmospheric emissions from a refinery and a coal-fired and oil-fired power plant was 20, 5.2, 28, respectively, displaying that the particles around the coal-fired power plant, as a coal-burning ambient environment, have a relatively low La/Sm ratio.

Hu (2016) reported that the La/Sm ratios in the particles from ambient indoor coal-burning environments in a lung cancer village in Xuanwei of Yunnan Province were from 4.95 to 8.29, averaged 6.55, indicating a relatively low La/Sm ratio for the emissions from coal-burning ambient environment. In the laboratory-designed coal-burning experiment in this study, it is shown that the La/Sm ratios in the particles emitted typically from burning the coals and briquettes are from 0.55 to 1.96, which are even lower than those in the coal-burning ambient environment. The relatively high La/Sm ratio in the ambient environment may be attributed to dilution by pollutants from other sources. The results in these studies showed that the particles emitted from burning coals in the laboratory has a relatively low La/Sm ratio, generally lower than 2.

In contrast to the results from coal-burning experiment in this study, the La/Sm ratio in the particles from gasoline-powered vehicles emissions showed a great different value. Xing (2018) studied the REEs in two particle samples emitted from gasoline-powered vehicles by engine test bench, and reported that the La/Sm ratios for two samples were 9.95 and 12.18 respectively. Hou (2017) studied the REEs in the particles from a highway tunnel dominated by gasoline-powered vehicles, and demonstrated that the La/Sm ratios in the airborne particles in the tunnel range from 11.63 to 25.14, similar to those from the engine test bench by Xing (2018). The results provided in Hou (2017) and Xing (2018) showed that the particles emitted by gasoline-powered vehicles could have a relatively high La/Sm ratio.

In Fig. 4, the comparison analysis indicates that the La/Sm ratios in the coal-burning particles are lower than 2, the La/Sm ratios in the particles in the ambient indoor coal-burning environments are between 4.95 and 8.29, and the La/Sm ratios in the particles form gasoline-powered vehicle emission are mostly higher than 9.95.

4. Conclusions

(1) The contents of total REEs in the coal-burning PM_{10} are lower than those in the briquette-burning PM_{10}. Similarly, the content of individual REE in the coal-burning PM10 is lower than that in the briquette-burning PM_{10}. The REEs in both cases are dominated by LREEs.
(2) The high equivalent mass concentrations of the coal-burning PM_{10} are closely related to the high volatile and thus low rank coals. In contrast, the high contents of the total REEs and total LREEs are associated with the high ash yields in raw coals.
(3) The La/Sm ratios in the particles emitted from burning the coals and briquettes, being lower than 2, are lower than those in the particles from gasoline-powered vehicle emission.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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