



Atmospheric Signature and Potential Sources of Rare Earth Elements in Size-Resolved Particulate Matter in a Megacity of China

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ABSTRACT

The atmospheric signature and potential sources of rare earth elements (REEs) in ambient particulate matter (PM) collected at urban (ZH) and background sites (ZWY) between February 2011 and January 2012 in the Yangtze River Delta region were investigated in this study. The average total concentrations of REEs for TSP, PM₁₀ and PM_{2.5} were measured to be 11.98, 9.37, 2.24 ng m⁻³ in ZH, which were 1.9, 1.8, 1.3 times higher than those measured in ZWY. The size distribution pattern of the REEs shows that they are significantly fractionated into coarse particles (e.g., approximately 50% in PM_{2.5-10}). However, La, Ce and Sm are even more enriched in PM with respect to each other and other REEs. It is also shown that Ce contamination is prevalent throughout the study area, which is particularly exemplified in the finer particulate matter fraction; this significant Ce contamination could be primarily attributed to vehicle emissions. Additionally, the REEs' pollution events during the sampling campaign were identified by the time series of the REE ratios. And the contaminations of La, Sm and Ce show clearly wind-induced variations. The enrichment factors for REEs indicate that La, Ce, Nd and Sm originated from a mix of anthropogenic and natural emission sources with small EF values.

Keywords: Aerosol chemistry; Particulate matter; REEs; Source.

INTRODUCTION

Ambient particulate matter (PM) pollution is a serious environmental problem particularly in developing countries that are experiencing rapid industrialization and urbanization. PM pollution has a negative effect on air quality and visibility; directly and indirectly influences regional and global climates; and affects public health; these effects are associated with the complexity of its composition (Guo *et al.*, 2014; Huang *et al.*, 2014). Considering the complex chemical constituents of PM pollution, PM pollution has been regarded as one of the most difficult challenges to solve in the field of environmental chemistry (Fanizza *et al.*, 2008). The measurement of the chemical constituents of ambient PM is critical to evaluate its environmental impact and potential sources (Villalobos *et al.*, 2015). Many studies have investigated the PM chemical constituents of water soluble ions (Eleftheriadis *et al.*, 2014; Wang *et al.*, 2015), carbonaceous components (Cao *et al.*, 2007; Jimenez *et al.*,

2009), heavy metals (Basha *et al.*, 2010; Wang *et al.*, 2013) and polycyclic aromatic hydrocarbon (PAHs) (Gao *et al.*, 2015; Liu *et al.*, 2015). However, information on rare earth elements (REEs) in PM is still sparse (Griffiths, 2010). REEs refer to the elements of Y, La and the lanthanides (i.e., Ce through Lu). These elements are generally split into two sub-groups: the cerium sub-group of “light” rare earth elements (LREE: La to Eu) and the yttrium sub-group of “heavy” rare earth elements (HREE: Gd to Lu, Y) (Jordens *et al.*, 2013). Several comprehensive case studies of atmospheric REEs have been conducted in some developed countries, such as America, Canada, Japan, the Netherlands and Spain (Kulkarni *et al.*, 2006; Moreno *et al.*, 2008; Suzuki *et al.*, 2011; Celo *et al.*, 2012). To the best of our knowledge, reports on the atmospheric REEs in China are limited and approximately 10 years old (Lu Peng *et al.*, 1997). China has the largest proved rare earth reserve of the world and is a major contribution country of REEs for the world's rare earth market (Zhao *et al.*, 2008). Along with the rapid and widespread application of REEs in industry, agriculture and medical materials in previous decades (Pang *et al.*, 2001; Wang *et al.*, 2001; Zhao *et al.*, 2008), it is necessary to measure their levels in ambient air.

REEs can accumulate in the human body and be deposited in organs via ingestion of food, inhalation of ambient PM

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and dermal contact (Koeberl and Bayer, 1992; Hao *et al.*, 2015). Several studies have noted that REEs follow hermetic, concentration-related trends, implying stimulatory or protective effects at low concentrations and detrimental effects at high concentrations (Zhao *et al.*, 2008; Pagano *et al.*, 2015). Many studies have reported that high concentrations of REEs may result in significant toxic effects on ecosystems and public health (Zhang *et al.*, 2001; Hao *et al.*, 2015). The adverse effects of exposure to high concentrations of REEs include growth inhibition, cytogenetic effects and organ-specific toxicity (Fanizza *et al.*, 2008; Pagano *et al.*, 2015). Research of occupational risks related to rare earth elements had shown a possible long-term risk of rare-earth pneumoconiosis in occupational workers based on a large accumulation of REEs in the lungs and lymph nodes of workers (Pietra *et al.*, 1984). Therefore, PM pollution is likely poses a significant threat to human health when exposure at high REE concentrations in the atmospheric environment. Additionally, PM toxicity depends on its aerodynamic diameters (Pope, 2000; Pope *et al.*, 2009). Thus, it is important to investigate the fractionations of atmospheric REEs in size-resolved PM to determine the adverse effects of REE pollution on human health and the environment risk.

Recently, several reports have investigated the enrichment of atmospheric REEs in total suspended particles (TSP) and PM₁₀ in the Bayan Obo mine region of China (Liang *et al.*, 2014; Wang and Liang, 2014; Wang *et al.*, 2014), which is the largest light rare earth deposit ever found worldwide. However, there is little information on the fractionation of increased atmospheric REE concentrations in cities without a nearby REE mine. Additionally, the natural geographical distribution pattern of rare earth ore in China shows that the fractionation trends of light rare earth ore are more prevalent in the northern areas than in the southern areas (Wen, 2012), while the geographical characteristics of REEs in the atmosphere are still unclear. To update the existing and potentially outdated information on REEs, we measured REE composition in size-resolved PM over a

one-year sampling campaign in a representative city in the Yangtze River Delta (YRD), which is one of the most polluted areas of China and the world.

The aims of this study are to (1) measure the concentration levels and size distribution patterns of REEs in size-resolved particles collected in China and make a global comparison of those data reported in previous studies; (2) describe the geochemical characteristic of REEs in three size fractions; (3) identify REE pollution events during the sampling campaign; and (4) analyze potential sources that may contribute to REE pollution.

METHODS

Sampling

The sampling area selected in this study was the city of Hangzhou (30°17'23.23"N, 120°08'55.95"E), which is the capital of Zhejiang province, is located at the southern wing of YRD region and is one of the three fastest growing economic development regions in China. At the end of 2013, the urban area of Hangzhou consisted of 3068 square kilometers with a population of 6.62 million long-term residents, and its gross domestic product (GDP) was 834.35 billion RMB. Hangzhou is considered to be a representative developed city in China and suffers from heavy haze pollution in recent years (Wang *et al.*, 2016). The sampling campaign of this study was conducted concurrently at two sites: an urban site on the rooftop (approximately 30 m high) of a residential building in the Zhaohui (ZH, 30°17'23"N, 120°9'24"E) district of the city center, which is surrounded by residential communities; and an urban background site (ZWY, 30°15'9"N, 120°07'28"E) in the Hangzhou Botanical Garden (approximately 5 m high) with no direct anthropogenic pollution emissions. The distance between the two sampling sites is over 6 kilometers, and the locations of the sampling sites are shown in Fig. 1.

At each site, TSP, PM₁₀ and PM_{2.5} were synchronized collected between February 2011 and January 2012. Each

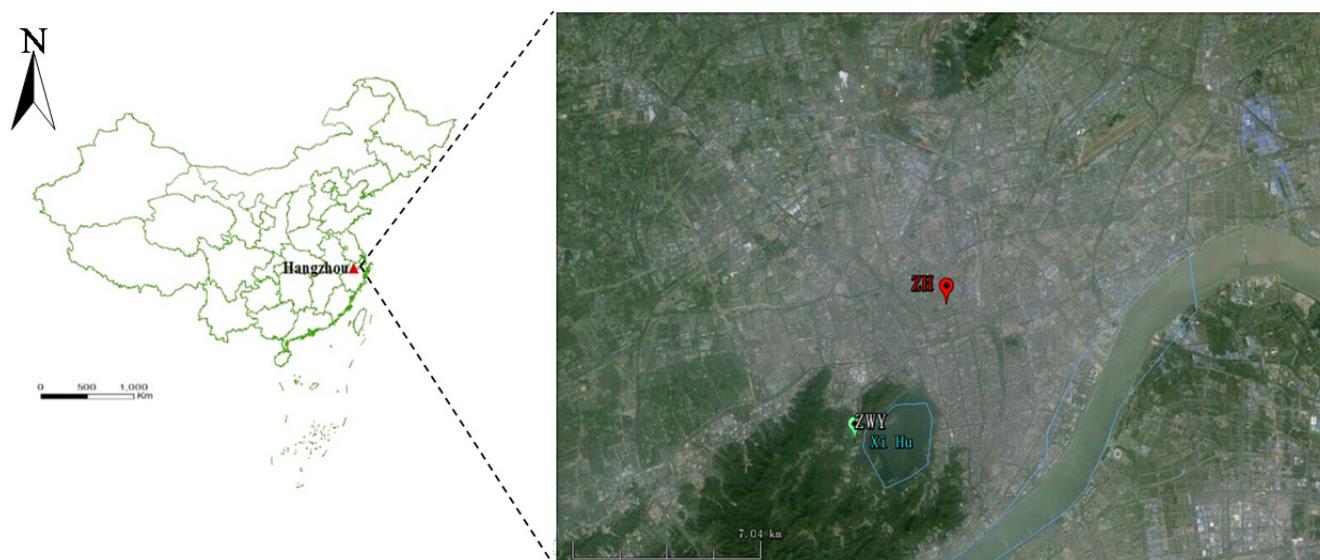


Fig. 1. Location of sampling sites. ZH: the urban site; ZWY: the background site.

sampling time began at 08:00 local time and continued for approximately 22 h. All samples were collected using medium-volume samplers (Wuhan Tianhong Intelligence Instrumentation Facility, TH-150 Medium Volume Sampler) operating at a flow rate of 100 L min⁻¹ with a 100, 10 and 2.5 cut-point impactor in parallel. Ambient PM was collected using acetate fiber filters (Ø 90 mm) with low blank levels for the REEs. Before and after sampling, all filters were conditioned for 48 h in darkened desiccators prior to gravimetric determination. Then the filters were weighted on an electronic microbalance (AX205, Mettler-Toledo, LLC, with a ±0.01 mg sensitivity) in a weighing lab under controlled temperature (20 ± 1°C) and relative humidity (RH) (40 ± 3%) conditions (Han *et al.*, 2015). The filters were sealed in polyethylene fiber boxes with a cover during transport to the sampling sites or back to the laboratory to avoid contamination (Dai *et al.*, 2016). After the sampling campaign, a total of 80, 68, 82 samples of TSP, PM₁₀ and PM_{2.5} were obtained after rejecting all invalid samples that occurred due to filter failure and contamination, sampler malfunctions or other unexpected accidents during sampling. The wind data were obtained from an open access website (<https://www.wunderground.com/history/>).

Chemical Analysis

The particulate matter samples were treated and analyzed by ICP-MS following a previously reported method (Shuai Qi *et al.*, 2005; Dai *et al.*, 2016). Each sampling filter was cut into small pieces using plastic scissors and placed in a 50-mL microwave digestion vessel with 10 mL HNO₃ (GR) and 3 mL H₂O₂ (GR). Then, the samples were digested using progressive settings, and subsequently, the leaching solution was transferred to a volumetric flask and diluted to 50 mL with deionized water. Inductively coupled plasma atomic emission spectroscopy (ICP 9000 (N+M) Thermo Electron Corporation, USA) was used to determine the concentrations of Al present in the samples (Han *et al.*, 2015). The determination of the REE concentrations was performed via inductively coupled plasma mass spectrometry (ICP-MS, Thermo, X serial, USA) (Kulkarni *et al.*, 2007a; Dai *et al.*, 2016). The measurement of duplicate samples and blanks constituted approximately 10% of all samples with a relative standard deviation of less than 5% on average. QA/QC in this study was implemented using sample blanks, analytical duplicates and a certified reference material (CRM). The accuracy and precision were ensured by GBW07303 from the National Research Center for Certified Reference Materials (Beijing, China) (Wang *et al.*, 2014). The recovery rates for REEs in the CRM were between 86 and 115%. Details on the analytical quality control and detection limits for analysis of REE in PM samples can be found in our previous publication (Dai *et al.*, 2016).

RESULTS AND DISCUSSION

REEs Concentrations and Fractionation in TSP, PM₁₀ and PM_{2.5}

REEs Concentrations

The REEs concentrations in TSP, PM₁₀ and PM_{2.5} at the

urban site (ZH) and the urban background site (ZWY) measured during the sampling periods are shown in Fig. 2. The concentrations of all of the individual REEs in ZH were obviously higher than those in ZWY. It is also shown in Fig. 2 that the average concentrations of REEs in the ZH and ZWY sites in Hangzhou followed the same order in TSP, PM₁₀ and PM_{2.5}: Ce > La > Nd > Y > Pr > Sm > Ga > Dy > Er > Yb > Eu > Ho > Tb > Tm > Lu. Additionally, the concentrations of a single REE in the atmospheric particulates conformed to the Oddo-Harkins distribution rule in crustal (Moreno *et al.*, 2008). The seasonal variation of REE concentrations in size-resolved particle samples collected at ZH and ZWY site was shown in Fig. S1 and another paper (Dai *et al.*, 2016). As for ZH site, the concentrations of REE decreased in the order of spring > winter > fall > summer. The seasonal trend of REE concentration at sampling site was likely attributed to micro-meteorological conditions and emission sources.

The total concentrations of REEs (Σ REE: Y, and La to Lu) for TSP, PM₁₀ and PM_{2.5} were 11.98, 9.37, 2.24 ng m⁻³ at the ZH site and 6.33, 5.27, 1.73 ng m⁻³ at the ZWY site. The Σ REE concentrations in TSP and PM₁₀ in this study were lower than those in Beijing (Wang *et al.*, 2001) and significantly lower than those in the atmospheric particulates around a mine in Baotou, which is known as the largest rare earth industrial base in China (Wang and Liang, 2014). The research data regarding REEs in the atmospheric environment of China in the literature are fairly limited, specifically with regard to PM_{2.5}. When compared to those reported at sites in other countries (Querol *et al.*, 2004; Kulkarni *et al.*, 2007b; Moreno *et al.*, 2008, 2011), the total concentration of REEs in Hangzhou (ZH or ZWY) is obviously higher (Table S5).

Size Distribution Patterns of REEs

The size distribution patterns of the REEs in TSP, PM₁₀ and PM_{2.5} are shown in Fig. 2. It is shown that REEs are significantly fractionated into coarse particles (approximately 50% in PM_{2.5-10}). The concentration ratios of REEs in PM_{2.5} to TSP at the ZH site are shown to be: Y (25%), La (26%), Ce (24%), Pr (42%), Nd (19%), Sm (44%), Eu (14%), Gd (17%), Tb (17%), Dy (19%), Ho (18%), Er (25%), Tm (21%), Yb (28%), and Lu (24%). At the ZWY site, all of these percentages are shown to have increased marginally. This result suggests that atmospheric REEs primarily exist in the coarse particles that may come from natural sources, such as weathered soils, rocks and re-suspended road dust.

Spatial Difference of REEs

Fig. 3 shows the spatial difference of atmospheric REEs in TSP, PM₁₀ and PM_{2.5} between the two sampling sites. The scatter plots of the REEs in TSP clearly show a trend at the ZH site; however, for the REEs in PM_{2.5}, the distribution patterns between the two sampling sites are not different except for a slight difference in Ce at the ZH site. Additionally, Ce is shown to be the most enriched element among the REEs tested at the ZH site, particularly for TSP and PM₁₀. Only the light rare elements of La, Y, Nd and Pr showed significant fractionations at the ZH site for TSP and PM₁₀. Furthermore, to explore the spatial

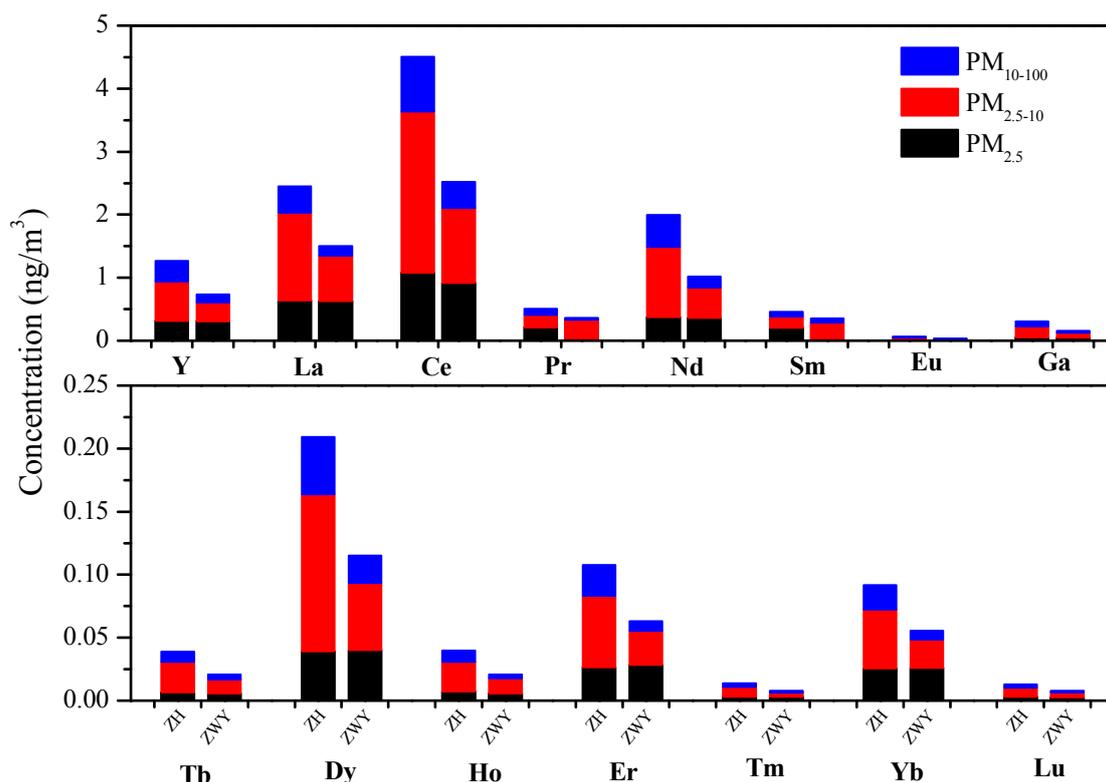


Fig. 2. Size distribution patterns of REEs in PM samples collected at Hangzhou.

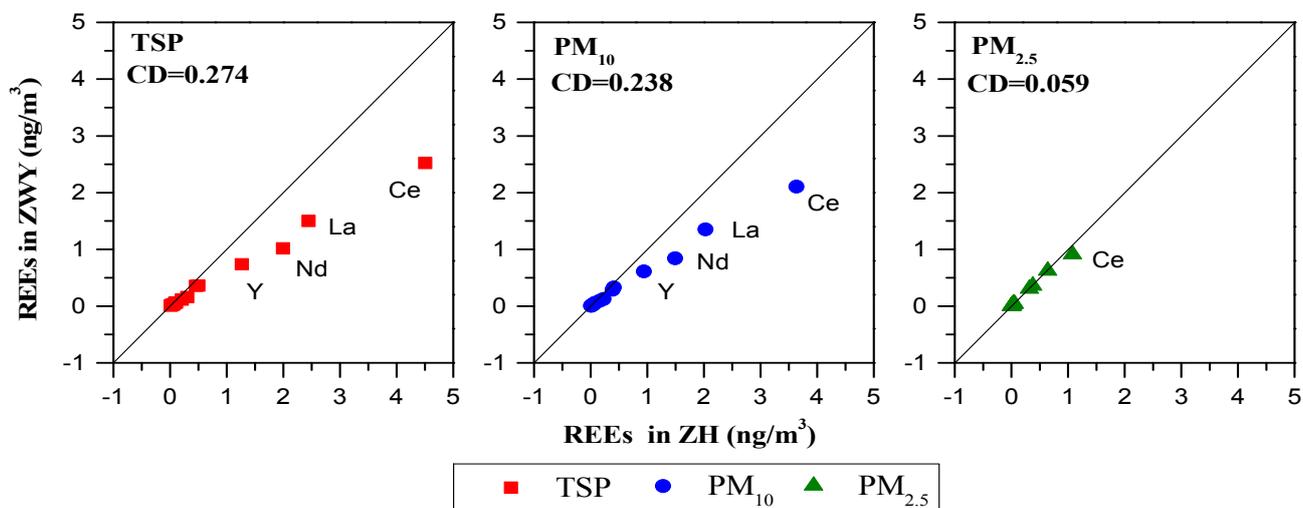


Fig. 3. The spatial difference of atmospheric REEs in TSP, PM_{10} and $PM_{2.5}$. CD is coefficient divergence between two sites.

variability of the determined concentrations of REEs in the PM collected at the two sites, we used a mathematical procedure known as the coefficient of divergence (CD) to normalize the wide variations in REEs concentrations. This method has been used widely in previous studies and is defined in Eq. (1) (Wongphatarakul *et al.*, 1998; Zhang and Friedlander, 2000; Wang *et al.*, 2013):

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

In Eq. (1), x_{ij} represents the average concentration for an REE component i of TSP (PM_{10} or $PM_{2.5}$); j and k represent the two different sampling sites; and p is the number of REEs. CD values near zero represent the uniformity of the REE particle composition between the two sampling sites; strong divergence is indicated when CD approaches one. Additionally, values of CD that are less than 0.2 suggest a relatively homogeneous spatial distribution.

CD values were calculated using the three different size fraction sets of the REE components. Fig. 3 shows that the REEs in TSP, PM_{10} and $PM_{2.5}$ between the two sampling sites exhibit significant spatial variabilities, where CD varies

from 0.059 to 0.274. All of the CD values of the REEs concentrations in the three size fractions are ordered as follows: $CD(TSP) > CD(PM_{10}) > CD(PM_{2.5})$. The highest CD value associated with TSP may be attributed to the fact that TSP is affected by several sources, such as industrial emissions and re-suspended dust. Only the REEs in $PM_{2.5}$ collected at ZH and ZWY sites are similar ($CD < 0.2$).

Geochemical Characteristics of Atmospheric REEs LREE/HREE

Generally, the ratio of LREE/HREE is used to measure the fractionation between LREEs and HREEs. In this study, LREE accounts for 82.7%, 83.1% and 91.4% of the total REE burden in TSP, PM_{10} and $PM_{2.5}$ at the ZH site, respectively. At the ZWY site, the ratios are marginally higher (84.3%, 84.7% and 93.0%, respectively). The ratios of LREE/HREE in this study are lower than those in northern China (e.g., ~ 21 Baotou and ~ 13 in Beijing), which is consistent with the distribution pattern of REEs in crust in China. Wang and Liang (2014) reported that the REEs in the atmospheric particles in Baotou originated from a light REE source that had relatively higher LREE/HREE ratios. According to the results of their study, the conspicuous lower LREE/HREE ratios found in Hangzhou indicated that Hangzhou may be affected by a heavy REE source. Similarly, due to the influence of light or heavy REE mine, the LREE/HREE ratios at sites in North America are similar to those in northern China, while both are higher than those at sites in Northern Europe (Moreno *et al.*, 2008; Wang *et al.*, 2001; Celo *et al.*, 2012; Bozlaker *et al.*, 2013).

REEs Ratios

REE ratios are another measure that can be used to analyze the geochemical signatures and identify the potential sources of REEs. In our samples, La, Ce and Sm are even more enriched with respect to each other and other REEs. Because the ZWY site is an urban background site, the REE ratios may reflect the natural atmospheric signature of REEs in Hangzhou. In addition to La/Yb and Ce/Yb, the scatter plots of La/Ce, La/Sm, Ce/Nd and Ce/Sm show a stable, uniform distribution near the crustal line along the vertical axis (Fig. 4). Compared to La/Sm (Ce/Sm) and La/Yb (Ce/Yb) values in the upper continental crust composition (UCC) (Taylor and McLennan, 1995), the samples with deviations indicated the fractionation of LREEs compared to HREEs in Hangzhou (see discussion in the preceding section). Fig. 4(a) shows that the La/Ce ratio at the ZH site tends to decrease marginally from the crustal value than the La/Sm and La/Yb ratios. The La-Yb scatter plots above the crustal line indicate La enrichment. Ce enrichment is also shown in Fig. 4, which shows a clear deviation in Ce/Yb between the natural crustal value and the uniform distribution of La/Ce. The La/Ce ratio at the ZH site tends to diverge from the crustal value (i.e., below the crustal line), particularly in the case of the TSP and PM_{10} samples. Additionally, there are appreciable La/Sm and Ce/Sm departures from crustal value at the ZH site, which show that Sm is also enriched to some degree. The Ce-Nd scatter plots in TSP and PM_{10} indicate that Nd is marginally enriched. The

deviation from the crustal values shows a clear correlation with particle size. The order of the deviation in the three PM size fractions are ordered as follows: $TSP > PM_{10} > PM_{2.5}$. This result is consistent with the results of the first section of this part, and both verify that coarse particles from anthropogenic emissions increase the REE abundance at the ZH site.

As shown in Table 1, the mean values of the La/Ce ratio at the ZH site (0.55 in TSP, 0.57 in PM_{10} and $PM_{2.5}$) were marginally lower than the crustal level (0.47); however, at the ZWY site, the values did not vary significantly. A similar pattern is also shown in the La/Sm ratio: the mean values of the La/Sm ratio at the ZH site for all three size fractions (6.09 in TSP, 6.62 in PM_{10} and 4.49 in $PM_{2.5}$) are also shown to be slightly lower than the crustal value (6.67), while the La/Sm ratio at the ZWY site are 6.77 in TSP and 8.05 in PM_{10} respectively, which is closer to the crustal value compared with those at ZH. The results indicate that the samples from the ZH site are marginally contaminated by La and Sm, particularly in the finer particles; these contaminations can attributed in part to industrial emissions in the vicinity of the ZH site such as municipal waste incineration (sewage sludge ashes) (Zhang *et al.*, 2001). Conversely, the mean values of Ce/Yb at the ZH site (50.27 in TSP, 50.57 in PM_{10} and 56.41 in $PM_{2.5}$) and at the ZWY site (52.70 in TSP, 50.43 in PM_{10} and 63.66 in $PM_{2.5}$) are nearly double the corresponding crustal value (29.09). Generally, an urban background site like ZWY is relatively unpolluted; however, the Ce/Yb ratio can be even higher than that at the ZH site. These findings indicate that Ce contamination is significant throughout the study area, particularly in the finer PM fraction. The literature shows that motor vehicles equipped with catalytic converters will emit particles containing REEs (Dodd *et al.*, 1991; Kitto *et al.*, 1992); higher enrichment factors for Ce and La in the particles exhausted from cars were found in Japan, and the automobile catalyst (SRM 2556) was highly enriched in Ce rather than La (Silva and Prather, 1997). However, a lower La/Ce ratio of 0.3 was observed in a rural area of Maryland near Deep Creek Lake that may be caused by motor vehicle emissions from highways because Ce and La were both added to catalytic converters in U.S.-made cars in the 1980s (Dodd *et al.*, 1991). The research results regarding vehicle emissions showed that $PM_{2.5}$ in highway tunnels exhibited lower La/Ce ratios of 0.2 (Kulkarni *et al.*, 2006). Along with the fast development of the economy and the urban expansion of Hangzhou in recent decades, the quantity of vehicles in Hangzhou now exceeds 2.5 million and is growing on average by more than 10% every year. Also, 1 in 3 or 4 people own a private car in Hangzhou, which is the highest ratio in China. Based on the knowledge of REE-bearing particle emissions from vehicles, significant Ce contamination at both sampling sites in Hangzhou could be attributed to vehicle emissions as well as crust input.

Identification of REEs Pollution Events

A time series variations of La/Ce, La/Sm and Ce/Yb ratios were analyzed to evaluate the REEs pollution events. In

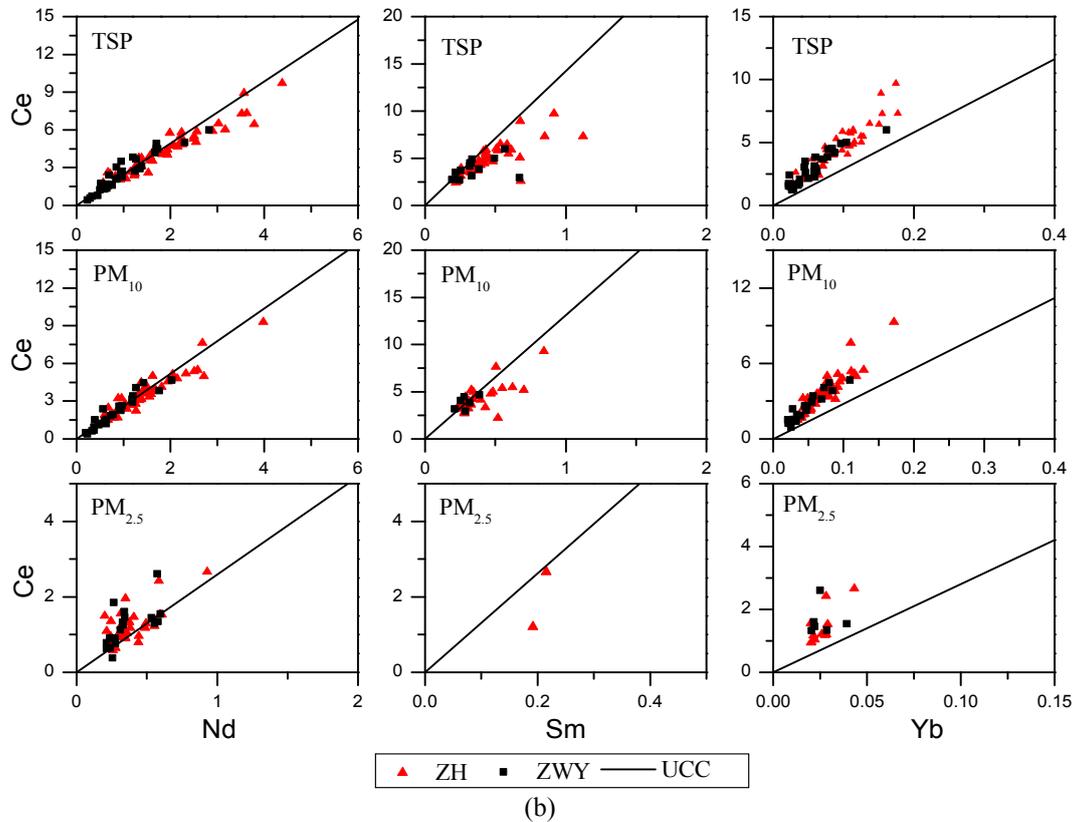
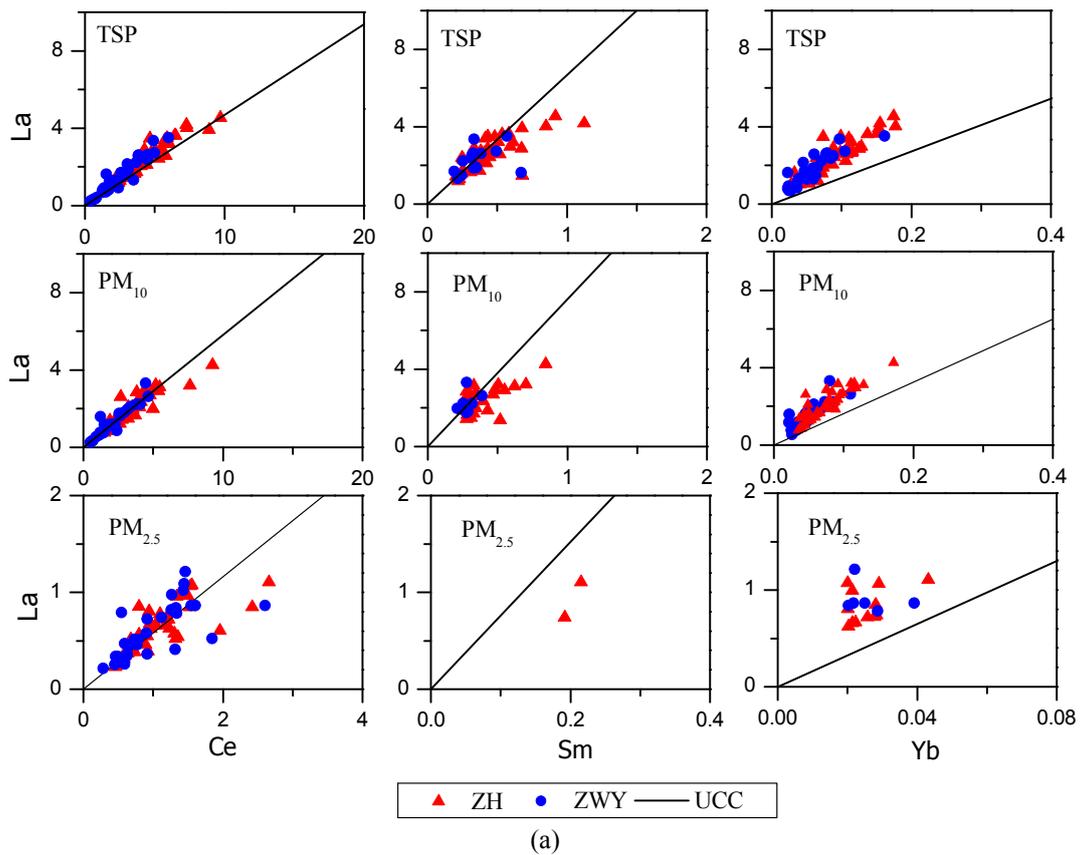


Fig. 4. (a) La/Ce, La/Sm and La/Yb plots for TSP, PM₁₀ and PM_{2.5} collected at both sampling sites; (b) Ce/Nd, Ce/Sm and Ce/Yb plots for TSP, PM₁₀ and PM_{2.5} collected at both sampling sites. UCC: upper continental crust (Taylor and McLennan, 1995).

Table 1. Ratios of REEs in TSP, PM₁₀ and PM_{2.5} collected at both sampling sites and UCC (Taylor and McLennan, 1995).

| | | La/Ce | La/Sm | La/Nd | La/Yb | Ce/Nd | Ce/Sm | Ce/Yb |
|-------------------|-----|-------|-------|-------|-------|-------|-------|-------|
| TSP | ZH | 0.55 | 6.09 | 1.30 | 27.62 | 2.36 | 11.19 | 50.27 |
| | ZWY | 0.59 | 6.77 | 1.48 | 32.11 | 2.47 | 11.12 | 52.70 |
| PM ₁₀ | ZH | 0.57 | 6.62 | 1.42 | 28.60 | 2.49 | 11.68 | 50.57 |
| | ZWY | 0.59 | 8.05 | 1.51 | 33.15 | 2.45 | 11.58 | 50.43 |
| PM _{2.5} | ZH | 0.57 | 4.49 | 1.89 | 33.74 | 3.23 | 9.31 | 56.41 |
| | ZWY | 0.53 | - | 1.99 | 35.96 | 3.46 | - | 63.66 |
| UCC | | 0.47 | 6.67 | 1.15 | 13.64 | 2.46 | 14.22 | 29.09 |

specific REE pollution events, for example, La contamination creates upward spikes in the La/Ce ratio, while Ce-bearing particle emissions produce downward spikes in La/Ce ratio. Significant sharp short-term fluctuations of the La/Ce, La/Sm and Ce/Yb ratios are shown in the REE pollution episodes during the sampling periods (Fig. 5).

The ratios during the sampling campaign at the ZH and ZWY sites showed a stable range of values in some cases. Additionally, significant differences in the variation patterns of the specific pollution events were also found. The strongest La enrichment appeared on 03/07/2012; there is a single peak in the La/Ce ratio on 02/07/2012 and a corresponding decrease on 04/07/2012 at both sampling sites (see the shadowed region of P1). Besides, the largest La/Ce ratio in P1 coincided with a higher level of the Ce/Yb and La/Sm ratios, which occurred during relatively high winds (approximately 10 m s⁻¹) along with the influence of NW winds in Hangzhou. In that scenario, the enhanced La concentration and slightly enhanced Ce concentration at the ZH and ZWY sites during P1 are linked to the transported air mass of La-related particles that probably originated from the anthropogenic emissions from the northwestern industrial area (Dai et al., 2015). At the urban background site, the ratios during this particular pollution event showed elevated levels at the ZWY site due to the relatively “clean” atmosphere. Other extended episodes (P3) of high La/Ce, La/Sm, Ce/Yb values were 3 days long and occurred simultaneously at both sites. During this period, there were predominantly NNE winds with a higher wind speed of 10 to 13 m s⁻¹. Different from the P1 event, the increased levels of La/Ce and Ce/Yb at the ZH site were more significant than those at the ZWY site. Considering the location of both sites, the enriched La and Ce concentrations at the ZWY site may result from the transport and dispersion of air polluted with La and Ce around the ZH site. Sm contamination primarily occurred during the P2 event (20/09/2012–21/09/2012) with at least 6 m s⁻¹ easterly winds. In this event, La/Ce and La/Sm showed simultaneous decreases, while Ce/Yb showed an upward spike, indicating that Sm was enhanced along with Ce.

Considering these three pollution events, Ce was always elevated, favoring the preceding assumption of the broad pollution of Ce in Hangzhou. The elevated levels of La/Ce, La/Sm and Ce/Yb in the associated increases and decreases during the P1, P2 and P3 events tend to vary with particle size and can be ordered as PM_{2.5} > PM₁₀ > TSP. Based on this discussion, the atmospheric signature of REEs is significantly related to their sources and weather conditions.

Source Analysis of REEs

There are many numerical methods for qualitatively or quantitatively identify source contributions of air pollutants, such as chemical mass balance model (CMB) (Bi et al., 2007; Adushkin et al., 2016), positive matrix factorization (PMF) (Liu et al., 2016), principle component analysis (PCA) (Dai et al., 2015), enrichment factors (EFs) (Dai et al., 2015), etc. In this study, the EFs combined with Pearson correlation analysis were used to discriminate the sources of atmospheric REE.

The inter-elemental correlations of REEs in TSP, PM₁₀ and PM_{2.5} collected at both sampling sites were analyzed using Pearson’s correlation coefficients (Tables S2–S4). All measured REE showed strong positive correlations ($R > 0.9$) with each other except La and Sm. The correlation coefficients of Sm with the other REE were considerably weaker, indicating that the source of Sm was different than the other REEs. The correlation coefficients of the REEs varied with particle size and were strong in TSP but rather weak in PM_{2.5}. These results suggested that REEs in fine particles originate from several sources, including industrial and vehicle emissions, while coarse particles may come from natural sources.

In this study, the enrichment factors of individual rare elements (R) in the atmosphere with respect to their soil abundances were calculated using aluminum (Al) as a reference element. The background value of Al, which is one of the most abundant elements in Chinese soil, was chosen to calculate the EFs in this study (Wei et al., 1990), as performed in previous studies (Hou et al., 2005; Reimann and de Caritat, 2005; Kara et al., 2014; Wang et al., 2014). The formula of the enrichment factor is described as:

$$EF(R) = \frac{[R]_{Air} / [Al]_{Air}}{[R]_{Soil} / [Al]_{Soil}} \quad (2)$$

A value of EF(R) near unity suggests a similar concentration pattern of $[R]$ in the atmosphere and soil, implying that natural soil is the predominant origin of the given pollutant. Generally, considering the local variation in soil composition, anthropogenic sources provide significant contributions to $[R]$ when EF(R) > 10. As shown in Fig. 6, La was the most enriched element at the ZWY site compared to the soil abundance, followed by Ce and Nd with EF means near 5. These findings were different at the ZH site, which showed the highest EF mean to occur with Sm, followed by La, Ce and Nd; this indicated that

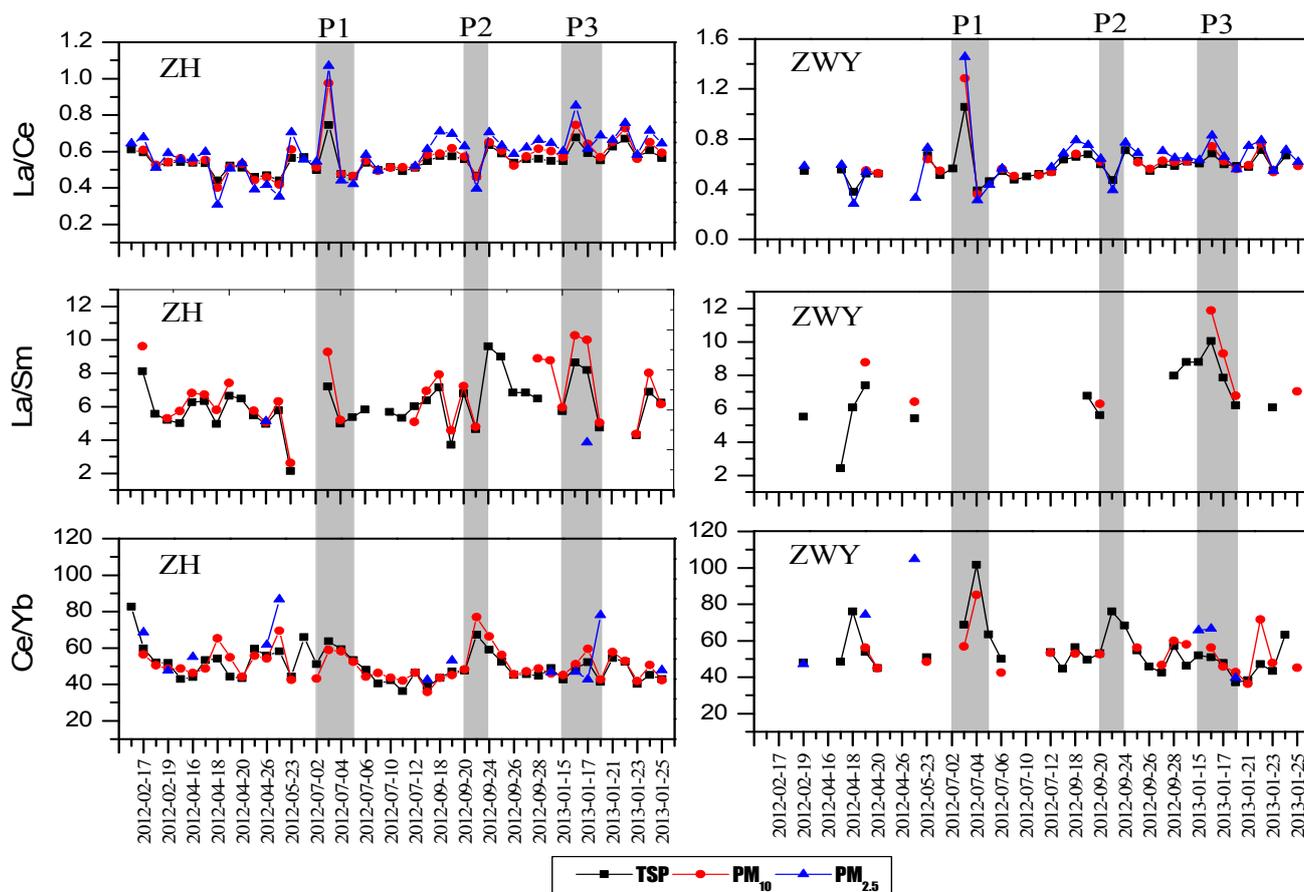


Fig. 5. Variations in La/Ce, La/Sm and Ce/Yb during sampling periods for TSP, PM₁₀ and PM_{2.5} at ZH and ZWY. P1, P2 and P3 were selected to analysis the strong transient variation of La/Ce, La/Sm and Ce/Yb during three pollution events (shadow regions).

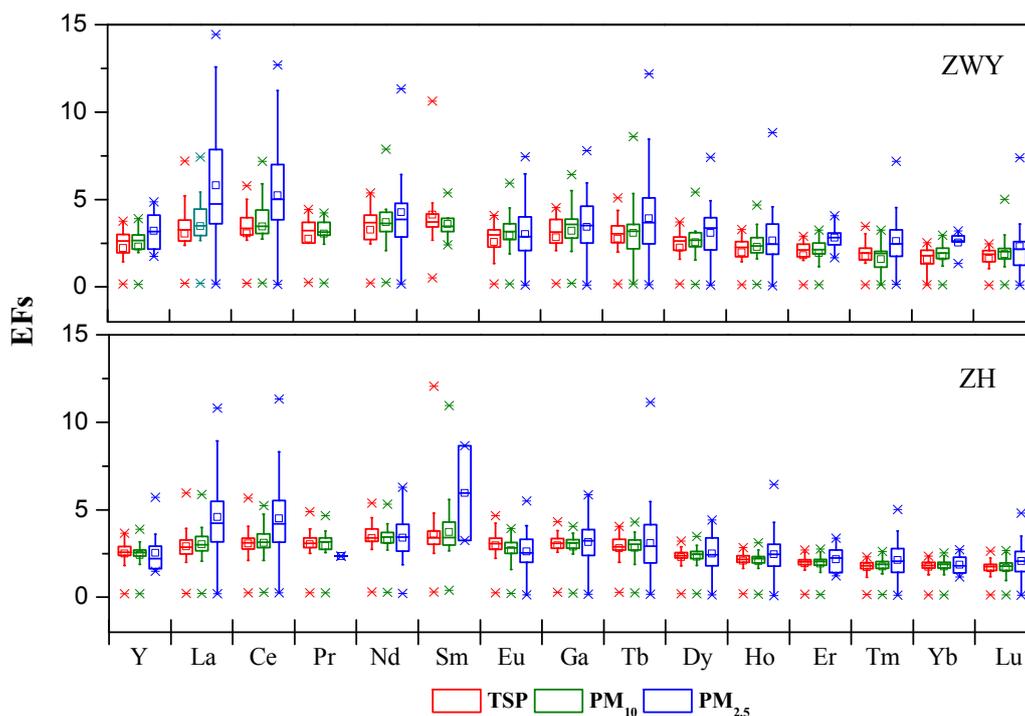


Fig. 6. Boxplots of enrichment factors for REEs in size-resolved particles collected at both sampling sites.

anthropogenic sources had more significant influence on Sm than on La and other elements at the ZH site. For the two sampling sites, the marginal enrichments of La, Ce, Nd and Sm with EF mean values near 5 indicated that these elements originated from a mix of anthropogenic and natural sources, including weathered soils and rocks. A clear pattern of enrichment is shown in Fig. 6, where the LREEs were more significantly enriched compared to the HREEs, which agrees with the results of previous studies (Kulkarni et al., 2006; Wang and Liang, 2014). The EF values of the REEs appear higher in the fine particles compared to the coarse particles; this can be explained by the fact that anthropogenic emissions probably have a significant contribution to the creation of fine particles containing REEs, while natural REEs are primarily more in coarser.

CONCLUSIONS

The total concentrations of REEs in TSP were 11.98 and 6.33 ng m⁻³, those in PM₁₀ were 9.37 and 5.27 ng m⁻³, and those in PM_{2.5} were 2.24 and 1.73 ng m⁻³ at the urban residential site (ZH) and at the urban background site (ZWY) in Hangzhou, respectively. The size distribution pattern of the REEs indicates that they are primarily fractionated into coarse particles (approximately 50% in PM_{2.5–10}). The ratios of LREE/HREE in this study are lower than those found in northern China (e.g., Baotou and Beijing), which is consistent with the geographic distribution pattern of REEs in crust in China. In this study, the elements La, Ce and Sm are shown to be more enriched compared to other REEs. The mean values of the La/Ce ratio for all three size fractions (0.55 in TSP, 0.57 in PM₁₀ and PM_{2.5}) and the La/Sm ratio (6.09 in TSP, 6.62 in PM₁₀ and 4.49 in PM_{2.5}) at the ZH site were both below the levels found in the upper continental crust. Additionally, it is shown that Ce contamination is prevalent in Hangzhou, particularly in the finer particulate matter fraction. The considerable Ce contamination in Hangzhou could be primarily attributed to vehicle emissions as well as crustal sources. Moreover, the specific REE pollution events were identified by analyzing the time-series variations of La/Ce, La/Sm and Ce/Yb. Considering the three REE pollution events that were observed during the sampling campaign, Ce was always elevated, and the elevated levels of La/Ce, La/Sm and Ce/Yb in both peaks and decreases during the three pollution episodes were variable with particle size and can be ordered as follows: PM_{2.5} > PM₁₀ > TSP. Moreover, the contaminations of La, Sm and Ce show clearly wind-induced variations. The enrichment factor for all REEs in TSP, PM₁₀ and PM_{2.5} indicated a slight enrichment of La, Ce, Nd and Sm, indicating that these REEs originated from a mix of anthropogenic and natural sources. Besides, LREEs were found to be significantly enriched compared to the HREEs.

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SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found in the online version at <http://www.aaqr.org>.

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