Rare earth elements in human hair from a mining area of China

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ABSTRACT

Rare earth minerals have been mined for more than 50 years in Inner Mongolia of China. In the mining area rare earth elements (REE) may be significantly accumulated in humans. Therefore, the aim of this paper is to characterize the REE concentrations in hair of local residents. REE concentrations in hair of 118 subjects were determined. The results showed that the mean concentrations of the determined REE in the hair of both females and males were usually higher from mining area than from control area. The mean concentrations of all the fifteen REE were much higher in hair of males than in hair of females from mining area. This suggested that males might be more sensitive to REE than females. In addition, the mean contents of the REE in hair of miners, particularly light REE (La, Ce, Pr and Nd), were usually much higher than the values in hair of non-miners from both mining area and control area, indicating that the miners were exposed to higher concentrations of REE in occupational environment. Among age groups, the relationships between REE concentrations and age groups showed that more and more concentrations of light REE accumulated in body of both females and males with age until 60 years, while heavy REE concentrations decreased with age in males who were exposed to low concentrations of heavy REE.

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1. Introduction

Rare earth elements (REE) usually refer to the elements spanning atomic numbers 57 (lanthanum) to 71 (lutetium). They have very similar physicochemical properties, and thus they form a chemically coherent group of elements. Sometimes, Yttrium is also included in the group (Ryu et al., 2007). In recent decades, REE were widely applied in agricultural, industrial and medicine field, hightechnology industries and others (Evans, 1990; Hirano and Suzuki, 1996). The increasing applications of REE and mining of rare earth mineral may emit abundant REE into environment. Consequently, enrichment of the REE induced environmental contamination, including soil contamination, hydrosphere contamination and biosphere contamination (Sultan and Shazili, 2009; Perez-Lopez et al., 2010; Tranchida et al., 2011; Delgado et al., 2012). Therefore, significant growths of interest in REE geochemistry have come out (Ryu et al., 2007).

Meanwhile, human health risk caused by environmental exposure to REE has obtained more and more attention in recent years. Low dose of REE have been shown to have the positive effects on the growth performance of animals and vegetables (He et al., 2003). It has been reported that REE exposure can improve the activity of telomerase and increase the percentage of cells in the

S-phrase and G2/M-phrase, and has no influence on the apoptosis of PBMNCs (Yu et al., 2007). However, animal experiments have indicated that in animals fed with REE diet, the REE can be absorbed through the digestive tract and can enter blood circulation. The REE can travel across the membrane into the erythrocytes (Wu et al., 2002). Chen et al. (2001) reported that REE could enter the cell and cell organelles and mainly be bound with biological macromolecules. Some functions of the cell in the human body may be deduced by REE (Chen et al., 2001). REE can induce low total serum protein (TSP), albumin, globulin, glutamic pyruvic transitanase, serum triglycerides, and immunoglobulin, but high cholesterol of blood. In addition, the influence of REE on males is a one-way irreversible process, whereas females show a strong ability of restoration (Zhang et al., 2000). Furthermore, it is reported that toxicity of REE varies from low to moderate levels. REE are non-essential elements for living systems. The long-term consumption of food contaminated with REE may cause chronic poisoning (Seishiro et al., 1996; Jiang et al., 2012). REE may be also accumulated in organs of human by ingestion, inhalation and dermal contact, and may induce some diseases. Long-term intake of low dose REE from environment may induce accumulation of REE in the bone structure. This may change the bone tissue and increase bone marrow micronucleus rate. Moreover, REE accumulated in bone can induce generation of genetic toxicity in bone marrow cell (Chen and Zhu, 2008; Zaichick et al., 2011). Zhuang et al. (1996) showed that the concentrations of Th, La, Ce, Gd, and Lu were significantly higher in tumor tissues

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compared with the normal brain tissues. This indicated that REE might be associated with tumor cells. In addition, REE can be accumulated in human brain through blood circulation, which can induce neurotoxic effects. Long-term ingestion of low dose REE can decrease the intelligence quotient of children and hinder the conduction of adult nervous centralis (Chen, 2005). Samochocka et al. (1984) suggested that REE are able to cross placental barrier and blood brain barrier. The infants can absorb abundant REE through breast milk (Samochocka et al., 1984). Therefore, the biological effects and distribution patterns of REE in the human body should be investigated.

Human biomonitoring does not provide comparative information on health before and after exposure, but it is much more accurate than environmental monitoring in providing data on health effects within the continuum "source emissions–environmental concentrations–exposure–human biomonitoring–health effects" (Reis et al., 2007; Li et al., 2012). Biomonitoring is therefore a useful complement to environmental monitoring for estimating the level of REE exposure. In recent studies, body fluids or tissues (saliva, blood, urine, hair, nails, etc.) have been widely used in the biomonitoring of heavy metals in large cohorts (Li et al., 2012, 2013). Compared with other biological specimen, such as blood and urine, hair is considered less invasive, more convenient for storage and transport to the laboratory for analysis, and less hazardous to handle. Many studies considered that the concentrations measured in hairs are not only the elements absorbed by organisms but also the elements adsorbed on the hair surface (Frisch and Schwartz, 2002; Harkins and Susten, 2003; Noguchi et al., 2012). Although there is a controversy on hair as biological indicators, hairs are an attractive biomonitoring substrate, at least superficially because of less invasive, more convenient. However, up to now, scientific data for REE in hairs is rather limited.

Within the context of the perspectives mentioned above, human health risk assessment of REE should be based on toxicology assessment and REE exposure of population assessment. Several studies have reported the concentrations of REE in human body (Chen et al., 2001; Yu et al., 2007). However, the reports about exposure of population assessment are rare (Arvela, 1979). Several investigations have shown that REE concentration in human hair can be defined as the index of REE exposure, which reflects the absorbed dose and load capacity of human body (Zhou et al., 1994). The investigations about REE in the human body and environment caused by a mining area from Inner Mongolia of China were hardly found at present. The rare earth mineral is mined through strip mining. Thus, the mining process can emit abundant REE into the environment. These REE can enter human body through environmental exposure to REE. The health of local residents may be influenced by these elements. Therefore, in order to characterize the REE concentrations in hair of residents and assess human health risk of REE from the mining area in Inner Mongolia, compared investigation of REE contents in human hair from the mining area and control area is conducted in this paper.

2. Materials and methods

2.1. Study area

The REE mining area, namely Baiyunebo iron-rare earth mineral deposit, was located in the central of the Inner Mongolia Autonomous Region of China and located in the northern of Baotou city (Fig. 1). The minerals exploited iron, REE, niobium and many other valuable mineral (Li, 2003). Approximately 54% of rare earth mineral over the world originate from Baiyunebo iron-rare earth mineral deposit (Li, 2008). The rare earth mineral mainly included monazite and bastnaesite, particularly enriched in light La, Ce, Pr and Nd (Gao, 2009). The area of the mining area was about 328 km^2. The mine has been operated since 1957. At present, mineral annual output is as high as 11 million tons.
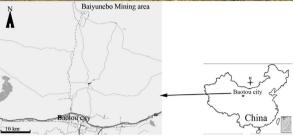

Fig. 1. The map of the study area.

2.2. Sampling

60 residents (33 females and 27 males) living in the vicinity of Baiyunebo mining area in Inner Mongolia of China were selected for hair sampling. The area was defined as mining area. The control area is located in the western part of Baotou city, which is about 200 km away from the Baiyunebo mining area (Fig. 1). The residents in the control area were hardly influenced by REE derived from the rare earth mine. 41 subjects (20 females and 21 males) living in the control area were selected for hair sampling. Moreover, another 17 subjects (13 males and 4 females), who are working in Baiyunebo mining area, were also selected for hair sampling. They are also living in the mining area. The ages of the individual are in the range of 11–77 years old. All of the subjects were living in the local area.

All of the subjects agreed to participate in this study. Additionally all recipients were informed that their hair will be used for REE determination. Therefore, hair sample was cut and collected from the nape of the head (close to the scalp) with scissors for each subject. Each collected hair sample was put into a paper envelope and labeled for the test.

2.3. Analysis methods

All the reagents were of analytical reagent grade or chromatographic grade. For dilution and wash, high-purity deionized water provided by a Milli-Q Plus filter apparatus (Millipore, MA, USA) was used throughout. All implements that came into contact with the samples had been prewashed using 5% nitric acid solution.

The individual hair samples were washed with detergent solution (2% non-ionic liquid detergent) and flushed with sufficient deionized water to remove exogenous matter. Then, the clean hair samples were dried in an oven for 10 h at 65 °C. The dried hair sample was cut into small pieces of 0.5–1 cm length. Approximately 0.2 g of each hair sample was weighed for digestion.

The weighed hair samples were digested with 3 ml concentrated nitric acid in cleaned glass tube at room temperature overnight. Then, the sample was further digested and heated at 100 ± 5 °C until no residue remained in the solution. The digested samples were cooled to room temperature and diluted to 25 ml with deionized water for further analysis. The blank was prepared in the same way but without the hair sample. All the reagents used were of ultrahigh purity. All the processes were conducted in clean laboratory.

The concentrations of the 15 REE, including lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), lutetium (Lu) and yttrium (Y), were determined by inductively coupled plasma mass spectrometry (ICP-MS). Considering the importance of quality assurance, a parallel routine check of the accuracy of quantified results was ensured through the use of Certified Reference Material (CRM, human hair powder GBW 09101 received from the National standard Sample Study Center, China). The contents of elements estimated in the CRM were found to be consistent with the values of elements reported in the CRM. The details of the method were