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Levels of rare earth elements, heavy metals and uranium in a population living in Baiyun Obo, Inner Mongolia, China: A pilot study

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HIGHLIGHTS

- Representing the first human biomonitoring study carried out in Baiyun Obo deposit.
- Levels of urinary REE, HMs and U were obtained in a population living in Baiyun Obo.
- HMs and U in the population increased concomitantly with increasing REE levels.
- Individual factors such as gender and age contributing to the inter-individual variation.
- Males and people in the young group were more sensitive to REE, HMs and U exposure.

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ABSTRACT

The Baiyun Obo deposit is the world's largest rare earth elements (REE) deposit. We aimed to investigate levels of REE, heavy metals (HMs) and uranium (U) based on morning urine samples in a population in Baiyun Obo and to assess the possible influence of rare earth mining processes on human exposure. In the mining area, elevated levels were found for the sum of the concentrations of light REE (LREE) and heavy REE (HREE) with mean values at 3.453 and 1.151 $\mu g\ g^{-1}$ creatinine, which were significantly higher than those in the control area. Concentrations of HMs and U in the population increased concomitantly with increasing REE levels. The results revealed that besides REE, HMs and U were produced with REE exploitation. Gender, age, educational level, alcohol and smoking habit were major factors contributing to inter-individual variation. Males were more exposed to these metals than females. Concentrations in people in the senior age group and those with only primary education were low. Drinking and smoking were associated with the levels of LREE, Cr, Cu, Cd and Pb in morning urine. Hence this study provides basic and useful information when addressing public and environmental health challenges in the areas where REE are mined and processed.

1. Introduction

Rare earth elements (REE) refer to the 15 lanthanides including lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu). Yttrium (Y) and scandium (Sc) are sometimes considered REE due to their similar chemical and toxicological properties, and because these elements are often found in the same ore deposits (Thomas et al., 2014). REE are frequently divided into two subgroups: light REE (LREE) and heavy REE (HREE) based on their physical and chemical separabilities as well as their ion radius (Pang et al., 2002). The LREE have in common increasing unpaired electrons, from 0 to 7, while the HREE are different from the LREE in that they have paired electrons (a clockwise and counter-clockwise spinning election). All the HREE adopt the hexagonal close-packed (hcp) crystal structure and all the LREE, with the exception of Sm, adopt the double *c*-axis hcp (dhcp) structure. Within each group, – chemical properties of the elements are very similar, with the result that they are always found together in mineral deposits. The LREE consists of the elements La, Ce, Pr, Nd, Pm, Sm and Eu, whereas the HREE com-

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prises the elements Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y. Pm, as one of the LREE, only occurs in trace quantities in nature as it has no long-lived or stable isotopes (Castor and Hedrick, 2006).

According to the British Geological Survey Database, the only countries known to be actively mining REE are China, Russia, India, Brazil and Malaysia. Among these countries, China has the largest REE production, accounting for more than 97% of the global supplies (BGS, 2011). REE are indispensable in many industries and technologies involving metallurgy, ceramics, magnets, petroleum, electronics, medical imagery, etc. (Castor and Hedrick, 2006; Hurst, 2010; Du and Graedel, 2013).

The global demand for REE is increasing annually and has led to the excessive exploitation of REE ores (Chen, 2011). Consequently, more REE are entering ecosystems through mining and processing as well as mine tailing wastes (Protano and Riccobono, 2002; Hu et al., 2006; Wang et al., 2008; Cai, 2012). REE in ores are generally by-products of iron, titanium, zircon, tin or sometimes U extraction (BGS, 2011). Additionally, the environmental issues associated with REE production are caused not only by REE but also by impurity components, especially radionuclides and heavy metals, in the REE-bearing ores. For example, xenotime (a rare earth phosphate mineral, whose major component is yttrium orthophosphate) in Malaysian placer deposits typically contains 2% U and 0.7% thorium. This was the main reason that the Malaysian processing industry failed and the plants were closed (BGS, 2011). The possible contaminants cause negative effects on aquatic and terrestrial organisms, as well as on humans. In some cases, they increase the mortality rates of aquatic and terrestrial organisms (Paul and Campbell, 2011; Rim et al., 2013).

The Baiyun Obo iron–REE–niobium deposit, located in Inner Mongolia, north China, is the world's largest REE deposit (BGS, 2011; Kanazawa and Kamitani, 2006; Wu, 2008), producing approximately 54% of the total global REE production (Li, 2008). According to China Daily refining one tonne of REE oxide can potentially produce 6×10^4 m^3 of waste gas, 200 m^3 of acidic water and 1.4 tonnes of radioactive waste. Intensive mining-refining operations and disposal of tailings piles in addition to litter governmental control have resulted in many crucial eco-environmental problems in Baiyun Obo district in the last few decades. Reports indicate that the contaminants associated with REE exploitation have been responsible for the pollution of local water, air and soil and the deterioration of the local grassland ecosystem (Hilsum, 2009; Meng et al., 2009; Guo et al., 2013; Wei et al., 2013; Xu et al., 2011).

Although there is no report of incidents of human REE poisoning through food consumption, concerns regarding potential effects of long-term exposure to REE on human health have been rising because REE can accumulate in blood, brain and bone after entering into the human body (Feng et al., 2000; Chen, 2005; Chen and Zhu, 2008; Rim et al., 2013). Previous epidemiological studies have identified the Baiyun Obo as one of the areas with the highest mortality rates due to malignant tumors in China (Zhang et al., 2001; Chen, 2005), suggesting that a combination of environmental, occupational and socio-economic factors may contribute to this health outcome. Unfortunately, despite the important eco-environmental deterioration caused by the mining activity, no biomonitoring study has been carried out in Baiyun Obo so far. This situation, together with the epidemiological finding mentioned above, were the basis of the present research focused on biomonitoring the exposure to pollutants related to REE production in a population in Baiyun Obo.

Urine is one of the most widely used and accepted mediums for biomonitoring environmental pollutants in occupational and environmental toxicology (Moon et al., 1999; Schroijen et al., 2008; Aguilera et al., 2010; Gil et al., 2011; Castano et al., 2012; Kitamura et al., 2012). Unlike hair, urine levels clearly reflect recent exposure. In addition, urine testing may substantially help in monitoring excessive exposure and appear to be suitable for use in prospective pilot studies as well as for identifying subgroups of population at increased risk in contaminated areas. In this study,

Table 1
Ceatinine adjusted urinary levels of REE, HMs and U in population living in the Baiyun Obo and the control area (μg g^{-1} creatinine).

	Baiyun Obo (*N* = 128)						Control area (*N* = 12)						*p*-value
	AM	GM	P 10	P 50	P 90	Max	AM	GM	P 10	P 50	P 90	Max	
La	0.101	0.068	0.025	0.067	0.208	0.858	0.025	0.019	0.006	0.019	0.055	0.055	0.021
Ce	0.138	0.083	0.020	0.078	0.361	0.796	0.020	0.016	0.007	0.017	0.031	0.037	0.009
Pr	0.039	0.027	0.011	0.026	0.080	0.501	0.011	0.008	0.004	0.008	0.022	0.031	0.072
Nd	0.181	0.135	0.057	0.134	0.369	2.307	0.044	0.035	0.020	0.047	0.066	0.088	0.034
Sm	0.044	0.034	0.014	0.034	0.089	0.261	0.015	0.011	0.003	0.014	0.025	0.027	0.006
Eu	0.020	0.016	0.007	0.017	0.038	0.067	0.007	0.005	0.003	0.005	0.010	0.025	<0.001
Gd	0.031	0.020	0.005	0.020	0.065	0.251	0.007	0.006	0.003	0.005	0.010	0.018	0.019
Tb	0.018	0.013	0.003	0.013	0.040	0.133	0.007	0.006	0.003	0.006	0.014	0.020	0.032
Dy	0.023	0.015	0.003	0.018	0.052	0.143	0.006	0.004	0.002	0.004	0.008	0.021	0.011
Ho	0.167	0.122	0.036	0.150	0.326	0.777	0.081	0.049	0.012	0.083	0.163	0.186	0.016
Er	0.013	0.010	0.003	0.009	0.025	0.075	0.004	0.003	0.002	0.003	0.006	0.006	0.003
Tm	0.003	0.002	0.002	0.002	0.004	0.010	0.002	0.002	0.002	0.002	0.002	0.002	0.133
Yb	0.008	0.005	0.003	0.006	0.015	0.115	0.004	0.003	0.002	0.003	0.008	0.009	0.225
Lu	0.003	0.003	0.002	0.002	0.005	0.017	0.002	0.002	0.002	0.002	0.003	0.003	0.169
Y	0.092	0.082	0.049	0.079	0.135	0.558	0.032	0.030	0.020	0.031	0.046	0.050	<0.001
Cr	2.885	2.739	1.787	2.812	3.967	6.149	1.224	1.142	0.725	1.135	1.824	2.348	<0.001
Mn	0.991	0.892	0.562	0.824	1.472	5.092	0.671	0.632	0.402	0.597	1.024	1.146	0.081
Ni	5.943	5.041	2.401	5.443	10.079	17.693	3.765	3.283	1.810	3.604	5.864	5.948	0.035
Cu	29.417	28.252	18.121	29.338	39.759	55.538	16.549	15.296	9.309	16.348	23.971	25.142	<0.001
As	27.832	24.925	14.099	25.106	41.146	126.088	13.497	12.161	6.473	10.639	20.991	27.103	0.002
Cd	0.483	0.392	0.152	0.388	1.020	1.816	0.227	0.199	0.094	0.212	0.348	0.551	0.011
Pb	1.650	1.250	0.517	1.318	3.024	10.001	0.723	0.460	0.103	0.687	1.525	1.853	0.014
U	0.084	0.058	0.016	0.061	0.193	0.436	0.018	0.011	0.002	0.013	0.035	0.054	0.001
∑LREE	0.523	0.403	0.197	0.368	1.125	3.453	0.121	0.106	0.048	0.127	0.187	0.196	0.005
∑HREE	0.358	0.318	0.162	0.312	0.581	1.151	0.144	0.124	0.067	0.155	0.223	0.262	<0.001
∑HMs	69.201	65.688	43.489	67.090	94.163	171.399	36.357	34.388	22.200	34.714	50.584	55.931	<0.001

AM, arithmetic mean; GM, geometric mean; P 10, 10 percentile; P 50, 50 percentile; P 90, 90 percentile; Max, maximum; ∑LREE, the sum of the concentrations of light rare earth elements (La to Eu); ∑HREE, the sum of the concentrations of heavy rare earth elements (Gd to Lu and Y); ∑HMs, the sum of the concentrations of selected heavy elements (Cr, Mn, Ni, Cu, As, Cd and Pb).