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Residual levels of Rare Earth Elements in Cereal and Their Health Risk Assessment from Mining Area in Jiangxi, South China

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Abstract The content of rare earth elements (REEs) in cereal were investigated, the risks of REEs exposure to human health were assessed. 428 cereal samples were collected from rare earth mining area and control area in Jiangxi, South China. The contents of 14 rare earth elements were determined by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The average concentrations of total rare earth elements in cereal from mining and control areas were 99.03 μg/kg and 34.21 μg/kg, and the difference was statistically significant (t=4.81, P=0.001). The Rice had the highest rare earth elements concentrations (102.79 μg/kg and 35.28 μg/kg for mining and control areas, respectively) and Maize had the lowest rare earth elements concentrations (76.98 μg/kg and 26.95 μg/kg for mining and control areas, respectively). The rare earth elements distribution patterns for both areas were characterized by enrichment of light rare earth elements. The health risk assessment demonstrated that the estimated daily intakes of rare earth elements through cereal consumption were considerably lower than the acceptable daily intake (70 μg/kg bw). The human health risks of REEs associated with cereal are low, but more attention should be paid to the effects of continuous exposure to rare earth elements on children.

Keywords: *rare earth elements, cereal, health risk assessment, ICP-MS, China REE mining areas*

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1. Introduction

Rare Earth Elements (REEs) are members of the group IIIB in the periodic table. The International Union of Pure and Applied Chemistry (IUPAC) defines the rare earth metals as a group of 17 elements consisting of the 15 lanthanoids [La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu] plus Sc and Y [1]. Commonly, La, Ce, Pr, Nd, Sm, Eu are indicated as light REE because of their atomic mass lower than 153 while Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu are indicated as heavy REE because of their atomic mass greater than 153.

REE was used in many applications in the past and it is becoming more popular in high-techindustry nowadays. REE is widely distributed in the biosphere. REEs can be accumulated in different areas of the environment following anthropogenic inputs because of the low mobility of these elements. Life processes (physiological and biochemical) of plants, soil, and living organisms are effected by rare earth elements [2-5]. REE effect enzyme activity, production, and intensity of photosynthesis, content of phytohormones, water regime of plants, and water deficiency resistance, and put effects on seed germination [6]. REE-based fertilizers increased the yield and quality of crops mostly used in China since the 1990's. Every year, about 50-100 million tons of REE-based salvolatile and phosphate fertilizers enter the agriculture system causing adverse health effects and detrimental environmental issues through bioaccumulation through the food chain [7]. In China, REE-accumulated plants enter the human food chain through different pathways causing danger to public health [8]. Small concentration ratio (CR) shows low transfer of REE from soil to plants. For humans, sample's acceptable daily intake (ADI) of rare earth nitrates is 0.2-2 mg/kg [9], a safety standard range of 12-120 mg/person/day [10]. Low level of REE in human tissues and fluids supports low transfer level of REE through food chain.

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 [11]. 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 [12]. Although there is no report on incidents of human poisoning through food chain, like other heavy metals, high concentrations of rare earth elements are likely to be harmful to plants and human health [13-16], and it has already been proven that long-term exposure of REE dust may cause pneumoconiosis in humans [17]. Besides these, people are increasingly interested in the impact of REE on children's neurodevelopment. Researches for children showed that REE might be related to decreased IQ and memory loss [18,19]. It is therefore necessary to investigate their concentration levels in major daily food of vegetable, cereal and meat to assess the potential risk of REE to human health.

The rare earth ore in present study is located in Dingnan County in the south of Jiangxi province and is one of the 11 national planned rare earth production areas, the rare earth reserves are approximately 1.10 million tonnes [20].

This is the first study dealing with REE in cereal of local households in close proximity to a large-scale rare earth mining site in Jiangxi, China. The main objectives were: (1) to investigate the levels of REE in cereal of mining and control areas in *Dingnan* County; (2) to evaluate the health risk of dietary REE exposure through cereal consumption.

2. Materials and Methods

2.1. Sampling and Pretreatment

The samples were collected from 10 sampling sites (5 from mining area and 5 from control area during September and November in 2016. The mining area is located in the vicinity of Dingnan rare earth ore and the control area was chosen from the site located 60 km away from the mining area. The living conditions, economic backgrounds and cultural and living habits are similar between the mining area and the control area. The natural environment is not affected by the rare earth mining area. The cereals were grown by the local residents and stored at house. Each sample was asked whether it was grown or bought in the market. The samples bought in the market were excluded. A total of 428 samples (edible part) including Rice, Maize and Legume were collected. Samples were washed with tap water and further washed three times with deionized water. Then, the samples were ground into powder in an agate mortar, passed through 0.149 mm nylon sieve, and stored at −20 °C until analysis was made.

2.2. Analytical Methods

The REEs concentration of all samples was determined by inductively coupled plasma mass spectrometry (ICP-MS, 7500CE, Agilent, Palo Alto, California, USA). The microwave digestion system was used for analysis where approximately 0.50g of the sample was weighed and digested with 8 ml of concentrated nitric acid (65%) in a PTFE digestion vessel. The solution was then poured into a volumetric flask and diluted to 10 ml with ultra-high purity water after cooling for about 40 min. The detailed measurement condition of ICP-MS was described by GB 5009.94-2012. REE concentration was expressed as μg/kg. External calibration was performed by measuring standard solutions obtained from national center of analysis and testing for nonferrous metals and electronic materials, China (NCATN). The standard solutions contained these 14 REE at 0, 0.05, 0.1, 0.5, 1, and 10 μg/L levels. Mixed solutions containing In, Rh, and Re obtained from NCATN were used as on-line internal standard at 1 μg/L level. The limits of detection (LOD) of these 14 REE for this method were 0.03-1.01μg/kg, which were determined as three times of standard deviation from seven blank solutions.

The accuracy and precision of the cereal analysis were assessed using Rice (GBW10010, national certifed reference materials of China). Standard solutions were inserted into the sample sequence every 8 samples to verify sensitivity and repeatability. The recoveries of REE were 88.2-98.6%.

2.3. Health Risk Assessment

The estimated daily intake of REE through cereal consumption was calculated according to Equation 1 [21].

$$EDI = \frac{C_V \times CR}{BW} \quad (1)$$

Here, EDI (μg/kg bw per day) represents the estimated daily intake of REE, Cv is level of REE in cereal (μg/kg), CR is consumption rate (kg/day), BW is body weight (kg). For analytical results below the LOD, 1/2LOD was used to produce estimates. Zhu *et al*., [22] have proposed a daily allowable intake of 70 μg/kg bw for rare earth oxides, which was certificated from human health survey in REE mining areas and animal experimental results.

2.4. Statistical Analyses

Statistical analyses for comparing the average results of different cereal samplings were performed using Student's t-test. $P<0.05$ was considered statistically significant. Statistical analysis was conducted using SPSS software package 16.0 (SPSS Inc., Chicago, IL, USA).

3. Results and Discussion

3.1. REE Levels in Cereal

The average concentration of REE for all 428 samples was 66.93 μg/kg. For cereal collected from mining and control areas, the average concentrations were 99.03 μg/kg and 34.21 μg/kg, respectively, and the difference was statistically significant ($t=4.81, P=0.001$). La, Ce, Pr and Sm were major elements and accounted for over 84% of total REE for mining area (Table 1). The total REE, light REE and heavy REE were statistically significant different between cereal from mining and control areas ($P < 0.05$). The results are consistent with previous studies, but the REE levels in the present study are relatively lower [23,24], The reasons for the differences in REE levels between different studies include the type of rare earth ore, REE levels in soils, and plant species. High concentration level of REE in soil can lead to more absorption and accumulation of REE [25]. Plant uptake of REE also depends on mobility and bioavailability of REE in soil [26,27]. Different type of rare earth ore has different mobility and bioavailability of REE influencing the absorption of REE.

3.2. REE Levels in Different Categories of Cereal

We divided the samples into three categories: Rice, Maize and Legume. For both mining and control areas, The REE concentrations of Rice were 130% higher than that of Maize. The Rice and Maize from mining area had significant higher REE concentrations than control area (P=0.01, P=0.004). Legume was no statistically significant difference in REE concentrations between mining and control area (Table 2). For both mining and control areas, the REE concentrations in cereal declined in the order of Rice > Legume > Maize. Previous studies had demonstrated the similar result [26,27]. Results of a study on REE absorption and distribution showed that the Rice had higher REE concentrations than Maize due to higher accumulation ability, but both plants show high concentration in roots [28,29]. Further analysis demonstrated that root tips of Rice and pea plants significantly show La and Yb in the xylem and endoderm [25]. This may be the reason that Maize has the lowest REE levels compared to Rice and Legume.

3.3. REE Distribution Pattern

The REE geochemistry of cereals from mining area and control are characterized by a relatively uniform chondrit-enormalized REE-pattern, with variable L/H (ΣLREE/ΣHREE= 6.38 to 8.59), significant LREE enrichment(($(La/Yb)_N$= 18.50 to 22.05) (Table 3). The values of δEu and δCe of mining area and value of δEu of control area were close to 1, but the value of δCe of control area indicated that there was a pronounced Ce-anomaly, (La/Sm)N and (Gd/Yb)N indicated that the internal differentiation status of light REE and heavy REE was moderate.

Mining area contains higher REE concentrations in comparison with control area. Although the REE abundances were different, the REE distribution patterns were similar for the two areas Figure 1. There was an obvious Nd anomaly in the distribution patterns. The reason might be the low Nd abundance in samples which is less than that in chondrites, resulting in a low ratio of sample/chondrite.

Table 1. REE concentrations in cereals from mining and control areas (μg/kg)

Element	Mining area		Control area		Total	
	Mean(μg kg^{-1})	SD	Mean(μg kg^{-1})	SD	Mean(μg kg^{-1})	SD
La	23.42	48.62	11.41	22.01	17.47	46.82
Ce	50.52	100.65	13.62	26.96	32.24	83.51
Pr	5.39	15.52	1.23	2.31	3.33	10.35
Nd	2.75	3.91	0.92	1.81	0.94	2.46
Sm	4.42	9.15	2.11	3.96	3.23	9.19
Eu	2.21	5.52	0.62	1.78	1.42	3.12
Gd	2.44	6.26	1.16	3.11	1.81	4.06
Tb	1.31	3.11	0.19	0.25	0.65	1.89
Dy	3.25	8.74	2.01	5.96	2.64	7.72
Ho	0.92	2.47	0.21	0.39	0.57	1.39
Er	1.16	3.12	0.69	1.49	0.93	1.82
Tm	0.22	1.84	0.05	0.11	0.34	0.67
Yb	0.855	2.79	0.35	0.72	1.01	2.12
Lu	0.17	0.99	0.03	0.08	0.40	1.12
LREE	88.71	193.56	29.91	62.45	58.63	121.31
HREE	10.33	29.32	4.69	12.11	8.34	20.80
ΣREE	99.03	189.37	34.21	57.45	66.93	144.02

Abbreviations: SD (standard deviation).

Table 2. Total REE concentrations in cereals from mining and control areas

Category	Mining area			Control area			t	p
	N	Mean(μg kg^{-1})	SD	N	Mean(μg kg^{-1})	SD		
Rice	156	102.79	201.46	150	35.28	58.21	4.02	0.010
Legume	36	97.45	192.94	40	34.19	63.21	1.88	0.067
Maize	24	76.98	79.62	22	26.95	40.41	3.04	0.004

Abbreviations: SD (standard deviation).

Table 3. REE characteristic values in cereals from mining and control areas

Area	L/H	δEu	δCe	$(La/Yb)_N$	$(La/Sm)_N$	$(Gd/Yb)_N$
Mining area	8.59	1.87	1.02	18.5	3.34	2.31
Control area	6.38	1.10	0.71	22.05	3.41	2.69

REE characteristic values in cereals from mining and control areas. Rare earth elements were Chondrite-normalized by Taylor & McLennan , [30] recommended chondrite abundance; L/H: light REE/heavy REE; (La/Sm)N and (Gd/Yb)N mean the internal diferentiation status of LREE and HREE, respectively; δEu, and δCe mean abnormality degree of Ce, and Eu. The subscript N refers to the relative abundance after chondrite was standardized: δCe=CeN/(LaN×PrN)/2, δEu= EuN/(SmN× GdN)/2

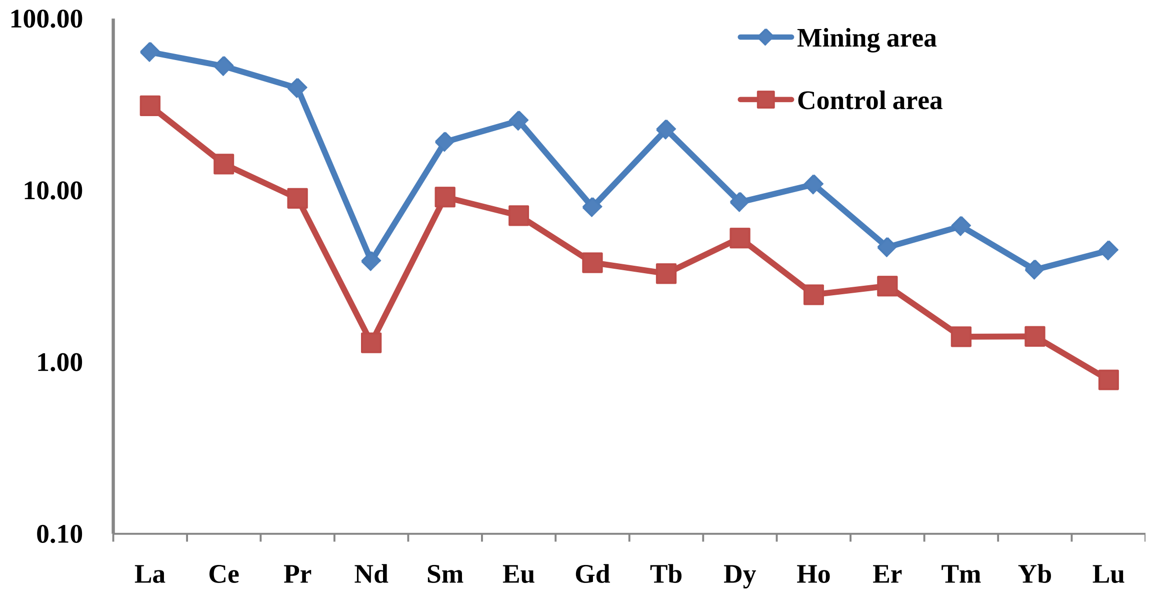

Figure 1. Chondrite-normalized REE distribution patterns for cereals. The REE abundances were normalized to those in chondrite, and then the pattern was achieved by plotting the ratios on a logarithmic scale against the atomic number. The REE in chondrite were assumed to be no fractionation. This could eliminate the abundant changes between odd and even atomic numbers.

3.4. REE Distribution Pattern

For different gender/age groups, the estimated daily intakes (EDI) of the total rare earth oxides were considerably lower than the established allowable daily intake (70 μg/kg bw), even calculated with 95% quantile of rare earth oxides in cereal, but children aged 2-12 years had higher EDI than the other group, especially the group of 2-7 years. The EDI of people over 13 years were substantially the same and had little variation (Table 4). Based on these results, the harm of REE exposure to adults through the consumption of these cereal is negligible. But more attention should be paid to the effects of continuous exposure to low levels of REE on human, especially on children 2-12 years old. In Jiangxi Province of China, rare earths mining activities are highly done and show strong correlation between the hairs of the mothers and their young children. Pair-comparison analysis for the means showed that the average hair level of five kinds of REEs in the young children was two times high as their mothers. Results indicate children living in nearby area found with maximum mean La concentration of 2202.9 ng/g that decreases with increase in distance from the mining sites. The levels of REEs in the hairs can be used as a biomarker to reflect body's level of exposure to REEs [31]. A study conducted in Fujian province also demonstrated that vegetable consumption would not result in exceeding the safe value of REE EDI for adults [32]. However, it is worth noting that children's neurodevelopment is more susceptible to REE that is related to decreased IQ and memory loss.

It should be noted that the health risk assessment results might be influenced by other factors such as other food (vegetables, meats, and fruits) ingestion and bioavailability of REE. The REE intake through dermal absorption and breath inhalation was not estimated. In addition, the data of consumption rate was obtained in 2007 and may have been changed after these years of economic development. Therefore, a more systematic risk assessment is needed.

Table 4. Estimated daily intake (μg/kg bw) of total rare earth oxides via cereal consumption in mining and control areas by different gender/age groups

Gender/age group	BW[a]	CR[a]	Mining area		Control area	
			EDI[b]	EDI[c]	EDI[b]	EDI[c]
2-7 years old	17.9	251.0	1.66	19.21	0.57	6.39
8-12 years old	33.1	400.5	1.44	16.67	0.50	5.51
Male, 13-19 years old	56.4	567.6	1.00	13.78	0.41	4.59
Female, 13-19 years old	50.0	462.4	1.10	12.71	0.38	4.21
Male, 20-50 years old	63.0	587.3	1.11	12.85	0.38	4.25
Female, 20-50 years old	56.0	497.8	1.05	12.22	0.36	4.05
Male, 51-65 years old	65.0	590.6	1.08	12.49	0.37	4.14
Female, 51-65 years old	58.0	501.2	1.03	11.88	0.35	3.94
Male, >65 years old	59.5	512.9	1.02	11.85	0.35	3.93
Female, >65 years old	52.0	405.3	0.92	10.71	0.32	3.55

Abbreviations: BW: body weight, CR: consumption rate, EDI: estimated daily intake. a Data were from the fourth China total diet study. b Calculated with median of rare earth oxides in cereal. c Calculated with 95% quantile of rare earth oxides in cereal.

4. Conclusion

The concentration of total REE in cereals from mining area is higher than that of control area. For both areas, REE concentration decreases in the order of Rice > Legume > Maize. The REE distribution patterns for both mining and control areas exhibit LREE enrichment trends. The health risk assessment demonstrated that the estimated daily intakes of rare earth elements through cereal consumption were significantly lower than the acceptable daily intake (70 μg/kg bw). The human health risks of REEs associated with cereal are low, but more attention should be paid to the effects of continuous exposure to rare earth elements on children.

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