Original Article

A Survey of 16 Rare Earth Elements in the Major Foods in China

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Abstract

Objective The aim of this survey was to investigate the level of contamination of the most consumed foods in China with 16 rare earth elements (REEs), and to provide the basic data for establishing and revising food safety standards for REEs.

Methods Sixteen REEs in foods were measured by inductively coupled plasma-mass spectrometry (ICP-MS) in the labs of the Centers for Disease Control and Prevention of four provinces and two municipalities, during 2009-2010.

Results 1 231 samples were analyzed and 19 121 concentration data of 16 REEs were collected. The REEs levels in the investigated foods varied significantly. The concentrations of cerium (Ce), dysprosium (Dy), yttrium (Y), lanthanum (La), and neodymium (Nd) were relatively high, while the remaining eleven REEs were at low levels. The mean values of total rare earth element oxides (REOs) in cereals, fresh vegetables, fresh aquatic products, fresh meats and eggs varied from 0.052 mg/kg to 0.337 mg/kg.

Conclusion 16 REEs in the major foods were at very low contamination levels in the investigated regions.

Key words: Rare earth elements; Food; Inductively coupled plasma-mass spectrometry (ICP-MS); China

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INTRODUCTION

Rare earth elements (REEs) are a type of heavy metals having low to moderate toxicity. REEs are non-essential elements for living systems. The long-term consumption of food contaminated with REEs may cause chronic poisoning[1-2]. Nevertheless, low doses of REEs have some beneficial effects on the physiological and biochemical responses of plants and animals. REEs are widely used as plant growth regulators for crops and as feed additives for livestock, poultry and aquaculture[3-5]. As a result, REEs from agriculture and the natural environment will be present in agricultural products, and be ingested by humans through the food chain. China is a leading country in the global production and use of REEs. Thus, it is necessary to systematically investigate the background levels of REEs in food, and to evaluate the impacts of these compounds on human health. The selectivity of the spectrophotometry method adopted by a previous survey was insufficient, and the concentrations of interfering elements such as calcium, magnesium, iron, and copper were much higher than the concentrations of REEs, making the accuracy of the data difficult to guarantee. Moreover, the limits of detection in that survey were not low enough, only five rare earth oxides (REOs) were analyzed, and the results reported only total REOs and not the individual concentration of each REO[6-7]. Compared with spectrophotometry, inductively

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coupled plasma-mass spectrometry (ICP-MS) has lower limits of detection, less interference issues, higher sensitivity, a wide linear concentration range, and the capability for multi-element determination. Hence, ICP-MS appears to be a more reliable option for the analysis of REEs. The concentrations of 11 REEs in cooked and mixed foods, analyzed by the ICP-MS method, were reported in previous studies[8-9]. In this study, the ICP-MS methodology was applied to determine the concentrations of 16 REEs in primary foods.

MATERIALS AND METHODS

Selected Areas

Six provincial areas were selected, including Beijing, Fujian, Guangdong, Hunan, Hubei and Shanghai.

Sampling

From 2009 to 2010, the six provincial Centers for Disease Control and Prevention corresponding to the selected areas chose five sampling points of prefecture-level cities in each area, and collected local food samples that were representative, typical, and fresh. Sampling sites included local supermarkets, farmers markets and shops. Collected samples included fresh vegetables (fresh edible fungi, leafy vegetables, fruiting vegetables, legume vegetables, brassica vegetables, and bulb vegetables), cereals (corn, rice, and wheat flour), fresh meat (pork, pig kidney, and pig liver), eggs (preserved duck eggs, fresh duck eggs, and chicken eggs), and aquatic products (mollusks, crustaceans, marine fish, and freshwater fish).

Analysis Methodology and Laboratory Quality Control

To ensure the accuracy and comparability of the data, we organized an expert group to develop unified standard operating procedures for the ICP-MS detection of 16 REEs in plant foods[10]. The 16 REEs analyzed were thulium (Tm), dysprosium (Dy), erbium (Er), gadolinium (Gd), holmium (Ho), neodymium (Nd), scandium (Sc), lanthanum (La), lutetium (Lu), praseodymium (Pr), samarium (Sm), cerium (Ce), terbium (Tb), yttrium (Y), ytterbium (Yb), and europium (Eu). Laboratory quality control procedures were implemented, and the results of the analyses were within two standard deviations.

Briefly, 0.5-2.0 g of food samples were digested and decomposed in a mixture of 10 mL nitric acid and 0.5 mL perchloric acid, with heating. Samples were digested until the solution appeared colorless or slightly yellow. Digested solutions were then removed from heat, cooled, and diluted with water to a volume of 10-25 mL. Finally, the 16 REEs were determined by ICP-MS, with rhodium (^{103}Rh), indium (^{115}In), and rhenium (^{185}Re) being used as on-line internal standards.

Data Collection and Analysis

Primary parameters of statistical analysis included the mean, median, 90th percentile, 95th percentile, 97.5th percentile, the maximum concentrations of 16 REEs in foods, and the number of samples.

The concentration of each common REO can be calculated from the concentration of each REE, and the sum of the 16 common REOs can be expressed as total REOs. The conversion factors were calculated using the following formula:

$$F=M[AmOn]/(m\cdot M[A])$$

Where: M[A] is the atomic weight of the REE, M[AmOn] is the molecular weight of the REO and m is the REE molar coefficient in the REO formula. Specific parameters are presented in Table 1.

Table 1. REEs, Common REOs, and Conversion Factors (to Obtain REO from REE)

Element A	Atomic Weight M	Oxide A_mO_n	Molecular Weight M	M	Conversion Factor F
Sc	44.96	Sc_2O_3	137.9	2	1.534
Y	88.91	Y_2O_3	225.8	2	1.270
La	138.9	La_2O_3	325.8	2	1.173
Ce	140.1	CeO_2	172.1	1	1.228
Pr	140.9	Pr_6O_{11}	1021.4	6	1.208
Nd	144.2	Nd_2O_3	336.4	2	1.166
Sm	150.4	Sm_2O_3	348.8	2	1.160
Eu	152.0	Eu_2O_3	352.0	2	1.158
Gd	157.3	Gd_2O_3	362.6	2	1.153
Tb	158.9	Tb_4O_7	747.6	4	1.176
Dy	162.5	Dy_2O_3	373.0	2	1.148
Ho	164.9	Ho_2O_3	377.8	2	1.146
Er	167.3	Er_2O_3	382.6	2	1.143
Tm	168.9	Tm_2O_3	385.8	2	1.142
Yb	173.0	Yb_2O_3	394.0	2	1.139
Lu	175.0	Lu_2O_3	398.0	2	1.137

RESULTS

Concentration Distribution of 16 REEs in the Major Foods in China

The results of the analysis of 16 REEs are listed in Table 2. The average contents of Dy, Ce, and La were between 0.0 524 mg/kg and 0.0 289 mg/kg (high level). In contrast, the average contents of Sc, Y, Er, Nd, Gd, and Pr were between 0.0 184 mg/kg and 0.0082 mg/kg (middle level), and the average contents of Sm, Yb, Ho, Eu, Tb, Tm, and Lu were between 0.0038 mg/kg and 0.0012 mg/ kg (low level). The sum of the 16 REOs from all the foods is shown as total REOs. The total REOs mean was 0.242 mg/kg. The median, 95th and 97.5th percentile were 0.016 mg/kg, 0.458 mg/kg, and 1.394mg/kg, respectively. These values indicate that the concentrations of REOs in the analyzed foods were relatively low.

Table 2. Results of the Survey of 16 REEs in the Major Foods in China

Elements	No. of Data	Median (μg/kg)	Mean (mg/kg)	90th Percentile (mg/kg)	95th Percentile (mg/kg)	97.5th Percentile (mg/kg)	Maximum (mg/kg)
Lu	1 176	<0.03	0.0012	1.00×10^{-4}	2.80×10^{-4}	6.00×10^{-4}	0.0191
Tm	1 196	<0.03	0.0013	1.20×10^{-4}	2.70×10^{-4}	6.90×10^{-4}	0.0215
Tb	1 183	<0.06	0.0014	3.50×10^{-4}	0.0012	0.0020	0.0581
Eu	1 182	<0.06	0.0017	7.80×10^{-4}	0.0016	0.0038	0.0690
Ho	1 113	<0.03	0.0018	3.00×10^{-4}	8.90×10^{-4}	0.0020	0.0672
Yb	1 184	<0.06	0.0019	6.80×10^{-4}	0.0016	0.0045	0.1260
Sm	1 231	<0. 2	0.0038	0.0022	0.0070	0.0154	0.2650
Pr	1 231	0. 2	0.0082	0.0048	0.0160	0.0388	1.6300
Gd	1 195	<0. 1	0.0117	0.0030	0.0109	0.0318	2.1900
Nd	1 195	0. 8	0.0124	0.0187	0.0472	0.0933	1.0300
Er	1 196	<0.06	0.0144	7.30×10^{-4}	0.0021	0.0053	14.900
Y	1 189	0.64	0.0169	0.0142	0.0432	0.0737	3.4700
Sc	1 192	8.3	0.0184	0.0298	0.0613	0.1210	1.0900
La	1 231	1.1	0.0289	0.0287	0.0750	0.1930	3.9900
Ce	1 231	2.9	0.0295	0.0494	0.0969	0.2180	1.8300
Dy	1 196	<0.08	0.0524	0.0034	0.0267	0.3900	4.5900
Total REEs	19 121	14	0.2060	0.1570	0.3920	1.1940	35.300
Total REOs	19 121	16	0.2420	0.1830	0.4580	1.3940	42.900

The results of the analysis of 16 REEs in fresh vegetables are shown in Table 3. In 486 fresh vegetables, the average contents of Ce, Dy, Y, La, Nd, and Sc were between 0.0502 mg/kg and 0.0218 mg/kg (high level). In contrast, the average contents of Er, Gd, Pr, and Sm were between 0.0107 mg/kg and 0.0062 mg/kg (middle level), and the average contents of Tm, Yb, Eu, Ho, Tb, and Lu were between 0.0038 mg/kg and 0.0027 mg/kg (low level).

Concentration Distribution of Total REOs according to Food Category

The total REOs means in fresh vegetables, aquatic products, fresh meats, eggs, and cereals were in the range between 0.052 mg/kg and 0.425 mg/kg. Fresh vegetables and aquatic products had higher total REOs means than other foods. Preserved duck eggs had a significantly higher total REOs mean than fresh eggs. Furthermore, processed aquatic products had a slightly higher total REOs mean than fresh aquatic products. For all foods, total REOs medians were lower than means. However, the 90th, 95th, and 97.5th percentiles were generally higher than means, except for fresh meats and fresh aquatic products, which had slightly higher means compared with their 90th percentiles. This suggests that total REOs in foods are not distributed normally. The results for the major food types consumed in China are presented in Table 4.

Table 3. Results of the Survey of 16 REEs in Fresh Vegetables

Elements	No. of Data	Mean (mg/kg)	Median (μg/kg)	90th Percentile (mg/kg)	95th Percentile (mg/kg)	97.5th Percentile (mg/kg)	Maximum (mg/kg)
Lu	463	0.0026	<0.03	1.50×10^{-4}	4.00×10^{-4}	1.00×10^{-3}	0.0191
Tm	476	0.0027	<0.03	1.20×10^{-4}	4.60×10^{-4}	1.00×10^{-3}	0.0215
Tb	476	0.0030	<0.06	5.40×10^{-4}	0.0019	0.0032	0.0581
Eu	477	0.0033	<0.06	9.10×10^{-4}	0.0017	0.0048	0.0690
Yb	477	0.0038	<0.06	9.40×10^{-4}	0.0033	0.0072	0.1260
Ho	408	0.0038	<0.03	5.90×10^{-4}	0.0018	0.0028	0.0672
Er	477	0.0040	<0.06	0.0011	0.0040	0.0069	0.1710
Sm	486	0.0062	<0. 2	0.0047	0.0130	0.0230	0.2650
Pr	486	0.0092	0.36	0.0135	0.0266	0.0524	0.4700
Gd	476	0.0107	<0. 1	0.0069	0.0170	0.0332	0.7610
Nd	476	0.0218	1. 8	0.0443	0.0886	0.1140	1.0300
Sc	476	0.0242	3.6	0.0322	0.1170	0.1840	1.0900
Y	476	0.0341	1.3	0.0394	0.0623	0.1050	3.4700
La	486	0.0479	2.2	0.0566	0.1410	0.3830	3.9900
Ce	486	0.0492	5.5	0.0884	0.1960	0.3440	1.8300
Dy	476	0.0502	<0.08	0.0060	0.0265	0.1300	4.5900

Table 4. Total REEs and Total REOs in the Major Foods in China

Food Categories	items	No. of Data	Mean (mg/kg)	Median (mg/kg)	90th Percentile (mg/kg)	95th Percentile (mg/Kg)	97.5th Percentile (mg/Kg)
Cereals	Total REEs	3 310	0.039	0.017	0.072	0.101	0.148
	Total REOs		0.052	0.024	0.097	0.133	0.192
Fresh vegetables	Total REEs	7 578	0.277	0.015	0.296	0.702	1.396
	Total REOs		0.337	0.019	0.368	0.881	1.729
Fresh meats	Total REEs	1 976	0.080	0.016	0.068	0.094	0.359
	Total REOs		0.098	0.023	0.088	0.122	0.427
Fresh eggs	Total REEs	890	0.048	0.018	0.083	0.130	0.154
	Total REOs		0.065	0.025	0.115	0.183	0.215
Preserved eggs	Total REEs	1 040	0.258	0.022	0.896	1.374	1.578
	Total REOs		0.306	0.031	1.042	1.600	1.841
Fresh aquatic products	Total REEs	4 199	0.283	0.013	0.154	0.701	2.196
	Total REOs		0.335	0.018	0.192	0.836	2.583
Processed aquatic products	Total REEs	128	0.352	0.488	0.516	0.516	0.516
	Total REOs		0.425	0.591	0.630	0.630	0.630

DISCUSSION

There have been several reports on methods to determine REEs in food[11-13]. However, surveys of the content of REEs in food are scarce[6,8-9,14]. A previous survey reported the concentrations of total REOs in common Chinese foods by three wavelength spectrophotometry, but the method could not distinguish interfering elements such as, calcium, magnesium, iron and copper, so the results are not comparable to the present survey[6]. The concentrations of lanthanides (Ce, La and Nd) in cultivated and wild-growing mushrooms have been investigated[14], as well as the concentrations of 15 REEs in kelp[15]. In a total dietary study, the concentrations of 11 REEs in twelve categories of cooked and mixed foods were determined by ICP-MS in four Chinese areas with different diet types[8-9].

This is the first survey using ICP-MS to determine the levels of 16 REEs (except promethium) in the most commonly consumed foods in China. As REEs are widely used in China's agricultural industry, the results of this survey will help to identify the REEs contaminating food.

In 1991, China developed standards to limit total REOs in cereals and vegetables. However, standards to limit the concentrations of total REOs in aquatic

products, fresh meats and eggs have not yet been established[16]. In cereals, the total REOs mean, median and 97.5th percentile were far lower than the national limit standard of 2.0 mg/kg. In fresh vegetables, the total REOs mean and median were lower than the standard limit of 0.7 mg/kg; however, the 95th and 97.5th percentiles were 0.881 mg/kg and 1.729 mg/kg, respectively, exceeding the standard limit. This indicates that it is necessary to further investigate the factors responsible for the increase in the concentrations of REOs in vegetables.

This survey provided basic data for risk assessment and for the revision of the Chinese food safety standards of REEs in 2010. This survey found that the concentrations of Ce, Dy, Y, La, and Nd were higher than the concentrations of other REEs, which may reflect the abundance of these elements in the soil. In addition, Ce, La, and Nd are also used in agriculture[4-5]. It is important that the revision or establishment of standardized limits for REEs takes into account those elements that were found at high concentrations. If necessary, a respective limit for each REE can also be established.

At present, as the toxicity mechanisms of REOs are still being studied, and all studies are focused on only a few REOs, the health risks of total REOs cannot be accurately assessed[17-18]. According to the food consumption data from the Chinese National Nutrition and Health Survey in 2002[19], the mean, median, and 90th percentile of the dietary intake of total REOs for an average Chinese adult were 133 μg, 17.8 μg, 156 μg, respectively. According to ADI (acceptable daily intake) from the research results by Zhu et al[20], the mean, median and 90th percentile of total REOs taken with the diet were 3.02%, 0.40%, and 3.54% of ADI, respectively. This suggests that the contamination risk of total REOs in common foods is very low.

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