SURVEILLANCE OF CONCENTRATIONS OF HARMFUL ELEMENTS IN FOODS PURCHASED IN AREAS AFFECTED BY THE GREAT EAST JAPAN EARTHQUAKE

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Introduction

Serious damage occurred on the Pacific coast of east Japan as a result of the tsunami and the subsequent Fukushima Daiichi nuclear disaster caused by the Great East Japan Earthquake on 11 March 2011. Various foods produced in East Japan were contaminated with radioactive materials. It is also possible that foods have been contaminated with other harmful substances such as heavy metal elements and harmful organic compounds released from industrial plants and dispersed widely into the environment by the tsunami. However, as far as we know, there have been few reports on food contamination with such harmful substances.

Here, we examined the possibility of food contamination with potentially harmful trace elements and heavy metal elements as a result of the tsunami. We used inductively coupled plasma mass spectrometry (ICP-MS) to survey the concentrations of 15 elements (Pb, Hg, Ba, Sb, Sn, Cd, Mo, Se, As, Ni, Co, Cr, V, Al, B) in food products purchased from markets located in the disaster area.

Materials and methods

Samples

From 2012 to 2013, squid and octopus, shrimp and crab, bivalve mollusks, fat greenling, flounder, mackerel, mushrooms, burdock, rice, taro, soybean, chicken, and pork were purchased from markets located in tsunami-stricken areas (Aomori, Iwate, Miyagi, Ibaraki, and Chiba prefectures). The total number of samples was 510. Each sample was homogenized uniformly in a food processor and stored at –20 °C until analysis.

Reagents

Double deionized water (Milli-Q 18.2 MΩ/cm resistivity; Merck Millipore, Darmstadt, Germany) was used for all dilutions. HNO_3 (specific gravity 1.40) for ultratrace analysis was purchased from Wako Pure Chemical Industries, Ltd. (Tokyo, Japan), and H_2O_2 (30%) of ultrapure quality was purchased from Kanto Chemical Co., Inc. (Tokyo, Japan). All vessels were of polypropylene; they were cleaned by being soaked in dilute HNO_3 and rinsed with distilled water before use. All solutions were appropriately diluted with 1% nitric acid solution unless otherwise stated. The element standard solutions used for calibration were prepared by diluting stock solutions of 1000 mg/L of each element (Kanto Chemical Co., Inc.). An internal standards solution was prepared by mixing solutions of Be, Ga, Y, In, and Tl, which were chosen as internal standards.

Instrumentation

An iCAP Q ICP-MS instrument (Thermo Fisher Scientific, Waltham, Mass., USA) was used[1], with the following conditions: Ar-auxiliary gas-flow rate 0.8 L/min; Ar-cooling gas-flow rate 14.0 L/min; quartz cyclonic chamber and perfluoroalkoxy alkane nebulizer (1.0 mL/min); water cooling; radiofrequency power 1550 W. The sensitivity and resolution of the apparatus were optimized by using a customized standard from Thermo Fisher Scientific. A deionized water sample was used to calibrate the instrument.

A Milestone Ethos-One (Milestone, Bergamo, Italy) closed-vessel microwave digestion system was used for sample preparation. Teflon reaction vessels were used in all the digestion procedures. The reaction vessels were cleaned with a mixture of 7 mL of HNO_3 (1.40), 1 mL of H_2O_2 (30%), and 0.5 mL deionized water before each digestion.

Digestion procedure and measurement

Food samples (0.5 g) were digested with 7 mL of HNO_3 (specific gravity 1.40) and 1 mL of H_2O_2 (30%) in a microwave digestion system for 31 min; 0.5 mL of the internal standards solution was then added and the

mixture was diluted to 50 mL with deionized water to prepare sample solutions. The operating program of the system was as follows: the temperature was raised from room temperature to 70 °C for 2 min, 50 °C for 1 min, and 200 °C for 15 min; it was then held at 200 °C for 10 min and cooled to room temperature over 60 min. Blank digests were performed for each Teflon reaction vessel used in the experiments in the same way. Fifty-four vessels were used.

The concentrations of 15 elements were quantified by measuring sample solutions by ICP-MS. The limits of quantitation (LOQs) achieved are shown in Table 1.

Table 1. Limits of quantitation (LOQs) of the method of analysis

Element	LOQ(mg/kg)	Element	LOQ(mg/kg)
B	0.23	Mo	0.0012
Al	0.15	Cd	0.000013
V	0.000039	Sn	0.0015
Cr	0.0034	Sb	0.00077
Co	0.00012	Ba	0.0050
Ni	0.0053	Hg	0.00024
As	0.0012	Pb	0.0063
Se	0.011		

Principal component analysis

The program SPSS (IBM, Armonk, New York, USA) was used. After standardization of, and calculation of a correlation matrix for, the analytical values for 12 elements (B, Al, V, Co, Ni, As, Se, Mo, Cd, Sn, Ba, Hg) for which the detection rate was above 50%, we performed a principal component analysis. First, we performed the analysis with a combination of element concentrations and all food groups. Next, in the same way, we performed the analysis with a combination of the concentrations of eight elements (V, Co, As, Se, Mo, Cd, Ba, Hg) and food groups for each area.

Results and discussion

Statistical data on the concentrations of elements in each food group are shown in Table 2. The concentrations of elements in food samples differed among food groups, and in some cases the detection percentages were very high (see below).

Boron

Of the 510 food samples, 371 contained boron at above the LOQ, giving a detection rate of about 73%. The maximum concentration was 32.7 mg/kg, in soybean. Soybean contain boron at higher average levels than in other food groups. Mushrooms also contained high levels, though not as high as in soybean.

Aluminum

There were 312 food samples that contained aluminum at above the LOQ, giving a detection rate of about 61%. The maximum concentration was 183 mg/kg, in soybean. The next-highest concentrations were in burdock, mushrooms, and bivalve mollusks.

Vanadium

All food samples contained vanadium. The maximum concentration was 3.16 mg/kg, in bivalve mollusks. The next-highest concentration was in shrimp and crab, and flounder.

Chromium

There were 219 food samples that contained chromium at above the LOQ, giving a detection rate of about 43%. The maximum concentration was 0.17 mg/kg, in soybean. The next-highest concentrations were detected in rice, mushrooms, and bivalve mollusks. The average chromium concentration in bivalve mollusks was 0.053 mg/kg (n = 21)—about double that in soybeans (0.027 mg/kg). This suggested that bivalve mollusks contained chromium at higher overall levels than in the other food groups investegated here.

Cobalt

There were 508 food samples that contained cobalt at above the LOQ, giving a detection rate of about 99%. The maximum concentration was 0.30 mg/kg, in bivalve mollusks. The next-highest was in shrimp and crab. Almost all of foods contained cobalt.

Nickel

There were 354 food samples containing nickel at above the LOQ, giving a detection rate of about 69%. The maximum concentration was 10.3 mg/kg, in soybean. Burdock and bivalve mollusks also contained nickel at relatively high levels.

Arsenic

There were 491 food samples that contained arsenic at above the LOQ, giving a detection rate of about 96%. The maximum concentration was 108 mg/kg, in flounder. The maximum concentration in flounder was a projected one. Excluding this value, the maximum concentration in flounder was 31.0 mg/kg. This value was comparable to the maximum concentrations in squid and octopus (31.1 mg/kg), shrimp and crab (22.7 mg/kg), and bivalve mollusks (27.3 mg/kg). In addition, seafood other than mackerel contained arsenic at higher levels than in other food groups.

Selenium

There were 390 food samples containing selenium at above the LOQ, giving a detection rate of about 76%. The maximum concentration was 1.8 mg/kg, in shrimp and crab. The concentration of selenium in seafood generally was higher than in the other food groups. All meats contained selenium. One sample of soybean contained selenium at a high concentration (1.3 mg/kg), but this value was a projected one.

Molybdenum

There were 504 food samples that contained molybdenum at above the LOQ, giving a detection rate of about 99%. The maximum concentration was 26.5 mg/kg, in soybean. Almost all of foods contained molybdenum.

Cadmium

There were 451 food samples containing cadmium at above the LOQ, giving a detection rate of about 88%. The maximum concentration was 5.9 mg/kg, in bivalve mollusks. In addition, the concentrations of cadmium in squid and octopus, shrimp and crab, and mushrooms were relatively high compared with those in other food groups. The maximum concentrations in these food groups were 1.3 mg/kg, 2.1 mg/kg, and 1.7 mg/kg, respectively.

The Food Standard for cadmium levels in rice in Japan is 0.4 mg/kg; analytical values above the standard were obtained from only 1 of 80 rice samples.

Tin

There were 303 food samples containing tin at above the LOQ, giving a detection rate of about 59%. The maximum concentration was 0.23 mg/kg, in mushrooms. The mushrooms contained tin at higher average levels than in other food groups.

Antimony

There were 125 food samples that contained antimony at above the LOQ, giving a detection rate of about 25%. The maximum concentration was 0.02 mg/kg, in pork. However, the average, minimum, and median values in pork were very low. Soybean and mushrooms contained antimony at low concentrations.

Barium

There were 431 food samples containing barium at above the LOQ, giving a detection rate of about 85%. The maximum concentration was 15.6 mg/kg, in soybean. Soybean and burdock contained barium at higher average levels than in other food groups.

Mercury

There were 428 food samples that contained mercury at above the LOQ, giving a detection rate of about 84%. The maximum concentration was 0.69 mg/kg, in fat greenling. Fat greenling and mackerel contained mercury at higher average levels than in other food groups.

Lead

There were 163 food samples containing lead at above the LOQ, giving a detection rate of about 32%. The maximum concentration was 0.14 mg/kg, in mushrooms. Bivalve mollusks, squid and octopus, and burdock contained lead at low concentrations.

When an individual food contaminated with harmful elements at clearly high levels was found frequently in the same food group, we considered that the contamination was a result of the tunami. We found here that the concentrations of harmful elements in the various food products purchased from markets located in tunami-striken areas were not clearly high.

The principal component analysis of the concentration data we obtained here clearly distinguished the fisheries products and the agricultural products. However, the differences in harmful element concentrations among the various food products did not become clear in our data analysis among the five tunami-stricken prefectures (Aomori, Iwate, Miyagi, Ibaraki, and Chiba prefectures). We are continuing to survey the element concentrations in food products sold in these areas so as to accumulate additional data and perform further analyses.

Table 2. Statistical data on the concentrations of each element in all the food groups

		Concentration (mg/kg)														
Food group		B	Al	V	Cr	Co	Ni	As	Se	Mo	Cd	Sn	Sb	Ba	Hg	Pb
Fat greenling	Min	0.232	0.158	0.001	0.004	0.001	0.005	0.703	0.191	0.000	0.000	0.002	0.001	0.006	0.039	0.007
	Max	0.842	0.524	0.024	0.004	0.005	0.012	11.700	1.110	0.001	0.006	0.010	0.001	0.058	0.687	0.007
	Average	0.406	0.301	0.008	0.004	0.002	0.009	2.850	0.390	0.001	0.001	0.004	0.001	0.017	0.173	0.007
	Median	0.314	0.288	0.004	0.004	0.002	0.010	2.280	0.346	0.001	0.001	0.003	0.001	0.013	0.111	0.007
Squid and Octopus	Min	0.312	0.166	0.000	0.003	0.001	0.006	0.786	0.212	0.003	0.003	0.002	0.001	0.005	0.007	0.006
	Max	1.730	22.900	0.059	0.022	0.015	0.041	31.100	1.090	0.049	1.310	0.066	0.006	0.027	0.078	0.056
	Average	1.220	4.180	0.021	0.008	0.006	0.019	5.540	0.498	0.011	0.258	0.008	0.002	0.020	0.046	0.016
	Median	1.200	0.422	0.010	0.005	0.004	0.017	2.880	0.447	0.008	0.142	0.004	0.001	0.012	0.040	0.013
Shrimp and Crab	Min	0.373	0.167	0.012	0.004	0.004	0.010	2.640	0.293	0.006	0.027	0.002	0.001	0.020	0.028	0.006
	Max	2.530	15.600	0.864	0.035	0.228	0.888	22.700	1.750	0.146	2.130	0.039	0.013	0.125	0.090	0.056
	Average	1.570	4.520	0.103	0.010	0.044	0.093	10.300	0.541	0.024	0.270	0.009	0.004	0.048	0.057	0.019
	Median	1.520	2.970	0.044	0.008	0.033	0.035	11.700	0.368	0.013	0.116	0.006	0.004	0.044	0.055	0.010
Bivalve mollusks	Min	0.440	0.303	0.007	0.010	0.007	0.009	0.344	0.081	0.007	0.000	0.002	0.001	0.023	0.002	0.008
	Max	4.810	45.800	3.160	0.087	0.302	1.650	27.400	0.587	0.242	5.880	0.022	0.008	1.380	0.210	0.118
	Average	3.310	14.300	0.420	0.053	0.094	0.532	4.900	0.271	0.091	1.360	0.009	0.003	0.231	0.024	0.044
	Median	3.730	10.400	0.198	0.065	0.055	0.399	1.680	0.276	0.082	0.217	0.008	0.002	0.177	0.009	0.031
Flounder	Min	0.260	0.150	0.001	0.006	0.000	0.006	1.020	0.235	0.000	0.000	0.002	0.001	0.005	0.018	0.007
	Max	0.728	1.770	0.425	0.006	0.0073	0.025	108.000	1.060	0.00593	0.0111	0.020	0.007	0.107	0.147	0.084
	Average	0.404	0.493	0.040	0.006	0.002	0.009	10.700	0.499	0.002	0.002	0.005	0.002	0.019	0.059	0.026
	Median	0.393	0.287	0.005	0.006	0.002	0.008	4.430	0.461	0.001	0.001	0.003	0.002	0.009	0.050	0.012
Mackerel	Min	0.235	0.147	0.003	0.003	0.003	0.005	0.815	0.423	0.000	0.001	0.002	-	0.005	0.028	0.009
	Max	0.545	1.180	0.030	0.012	0.011	0.012	2.670	1.030	0.0743	0.017	0.051	-	0.141	0.495	0.009
	Average	0.331	0.438	0.011	0.008	0.008	0.007	1.600	0.728	0.005	0.009	0.008	-	0.021	0.232	0.009
	Median	0.293	0.213	0.009	0.008	0.008	0.006	1.530	0.736	0.002	0.008	0.006	-	0.010	0.209	0.009
Mushrooms	Min	0.479	0.263	0.001	0.006	0.000	0.006	0.006	0.013	0.003	0.007	0.002	0.001	0.019	0.001	0.011
	Max	20.700	39.800	0.111	0.130	0.0777	0.138	0.162	0.402	0.131	1.790	0.227	0.007	1.190	0.365	0.144
	Average	5.830	9.020	0.023	0.029	0.016	0.037	0.038	0.083	0.033	0.406	0.026	0.003	0.292	0.040	0.048
	Median	2.130	4.050	0.014	0.022	0.008	0.019	0.015	0.054	0.014	0.123	0.011	0.002	0.219	0.009	0.034
Burdock	Min	1.560	0.151	0.000	0.004	0.002	0.010	0.000	0.014	0.003	0.006	0.002	0.001	0.061	0.0004	0.006
	Max	2.460	87.500	0.1220	0.045	0.045	2.110	0.09450	0.135	0.323	0.219	0.017	0.002	6.300	0.0004	0.145
	Average	1.880	9.110	0.022	0.012	0.017	0.282	0.014	0.075	0.034	0.046	0.006	0.001	1.630	0.0004	0.019
	Median	1.830	2.920	0.009	0.008	0.014	0.101	0.007	0.075	0.017	0.037	0.004	0.001	1.290	0.0004	0.012
Rice	Min	0.303	0.150	0.000	0.004	0.001	0.013	0.040	0.011	0.281	0.001	0.002	0.001	0.014	0.001	0.007
	Max	1.280	4.850	0.0124	0.080	0.020	0.737	0.245	0.105	1.090	0.411	0.027	0.001	0.627	0.011	0.038
	Average	0.514	0.688	0.001	0.013	0.005	0.090	0.114	0.025	0.612	0.044	0.006	0.001	0.096	0.002	0.014
	Median	0.444	0.360	0.001	0.008	0.004	0.069	0.110	0.019	0.599	0.016	0.004	0.001	0.059	0.002	0.008
Taro	Min	0.783	0.168	0.000	0.003	0.002	0.015	0.000	-	0.005	0.003	0.002	0.001	0.049	0.000	0.007
	Max	1.750	6.050	0.0198	0.011	0.045	0.561	0.015	-	0.195	0.184	0.047	0.001	2.990	0.0020	0.007
	Average	1.050	2.040	0.005	0.006	0.012	0.128	0.003	-	0.083	0.041	0.012	0.001	0.587	0.001	0.007
	Median	1.010	1.290	0.003	0.005	0.010	0.092	0.002	-	0.080	0.023	0.006	0.001	0.296	0.0004	0.007
Soybeen	Min	19.100	0.411	0.002	0.004	0.025	0.242	0.001	0.011	0.384	0.018	0.002	0.001	0.353	0.000	0.006
	Max	32.700	183.000	0.108	0.168	0.307	10.300	0.018	1.280	26.500	0.173	0.090	0.003	15.600	0.0049	0.051
	Average	25.700	20.600	0.023	0.027	0.092	2.050	0.006	0.079	7.160	0.070	0.015	0.001	3.430	0.001	0.014
	Median	25.600	10.200	0.018	0.017	0.067	1.580	0.005	0.033	3.950	0.056	0.006	0.001	3.410	0.0004	0.011
Chicken	Min	-	0.200	0.000	0.003	0.000	0.006	0.000	0.074	0.007	0.000	0.002	0.001	0.005	0.000	-
	Max	-	0.200	0.00278	0.013	0.0164	0.006	0.234	0.583	0.638	0.01790	0.041	0.001	0.031	0.0446	-
	Average	-	0.200	0.001	0.006	0.001	0.006	0.040	0.169	0.040	0.001	0.005	0.001	0.014	0.007	-
	Median	-	0.200	0.001	0.006	0.001	0.006	0.005	0.160	0.024	0.0002	0.003	0.001	0.011	0.002	-
Pork	Min	0.542	0.170	0.000	0.004	0.000	0.005	0.000	0.128	0.005	0.000	0.002	0.020	0.007	0.000	0.023
	Max	0.542	0.257	0.0017	0.049	0.0008	0.069	0.0247	0.327	0.017	0.00052	0.029	0.020	0.030	0.020	0.023
	Average	0.542	0.207	0.001	0.015	0.0005	0.022	0.005	0.203	0.008	0.0002	0.003	0.020	0.014	0.004	0.023
	Median	0.542	0.201	0.001	0.008	0.000	0.017	0.001	0.199	0.007	0.00005	0.002	0.020	0.010	0.002	0.023

(-): The value is below LOQ

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References:
1. Katrin L., Jana N., Carsten K., Kristian M., Stephan W., Frank K., Erik H.L. (2013); *Anal. Bioanal. Chem*. 405(25): 1184-9