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TOXIC AND TRACE ELEMENTS IN FOODSTUFFS IN JAPAN

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INTRODUCTION

From the view point of environmental safety assessment it is important to have information on the levels of toxic and trace elements in foodstuffs. It is also essential to develop suitable analytical methods for these elements in order to obtain accurate analytical data.

In this paper, we have used two analytical methods, inductively-coupled plasma atomic emission spectrometry (ICP-AES) and neutron activation analysis (NAA), for analysing toxic and trace elements in several food samples.

MATERIALS AND METHODS

Food samples were collected from the markets and farms of non-pollution area in Ibaraki-Prefecture, Japan. Some of rice samples (code name: Hojo) was cultivated in our institute. Samples were analysed by NAA and ICP-AES.

NAA: Dried samples (100-200 mg) were sealed in quartz ampoules made from synthesized silica (Toshiba T-4040). The samples were irradiated in the JRR-4 Reactor, Ibaraki, at a neutron flux density of 5.5 X 10^{13} n/cm/s for 1 to 5 hours. After about 5-day cooling period As-76, Br-82 and K-42 were measured with Ge detector in combination with a multichannel analyzer (SEIKO EG&G 7800). Isotopes with longer half-lifes, Zn-65, Se-75, Hg-203, Cr-51, Fe-59, Co-60, Rb-86 and Cs-137 were measured after about 40-day cooling period.

For the determination of Hg, some samples were heated in a quartz tube under O_2 and N_2 streams and the evaporated Hg was collected with an activated charcoal trap which was measured.

ICP-AES: Dried samples (200-1000 mg) were decomposed with HNO_3 in teflon bombs at 130 ℃ for about 4 hours. The sample solution was heated on a hotplate with addition of HNO_3 and $HClO_4$ (0.5-1 ml) until the fumes of $HClO_4$ occured. Then HNO_3 (1 ml) was added to the sample and diluted to 50 ml. Shimadzu ICPV-1000 was used for the analysis of Zn, Cu, Fe, Mn, Ba, Sr, Mg, Ca, P and K.

The methods were checked by analysing standard reference materials, e.g. IAEA: Horse Kidney, Fish Flesh, NBS: Orchard Leaves, Tomato Leaves.

RESULTS AND DISCUSSION

Analytical results obtained by NAA and ICP-AES for food samples are shown in Table-1 and -2, respectively.

Zn, (Se), Fe, Rb, Cs, Br and K were measured by INAA in many kinds of food samples, and As and Se was detected in several marine foods. Hg was only detected in tuna by instrumental method (INAA). Therefore, some samples was heated and the evaporated Hg was collected with activated charcoal. Hg was successfully separated from Se and other elements and determined in fish samples. Concentrations of Cr, Co and Cs in several samples are near the limit of detection. Therefore, the analytical accuracy for these element thought to be not so sufficient.

Zn, Cu, Fe, Mn, Ba, Sr, Mg, Ca, P and K were detected by ICP-AES. It was tried to measure Cd and Pb in food samples by this method. However, concentrations of Cd and Pb in the samples were under the limit of detection due to the interferences of major elements such as Mg, Ca, K, Na etc.

The elements, Zn, Fe and K were detected by the two method. Values for Zn by ICP-AES was somewhat higher than those by NAA. This may be due to the effect of Mg interference in the ICP-AES measurement. However, the differences of the values for Zn, Fe and K obtained by these two methods were, in most cases, within 15%.

It was observed that marine products contained high amounts of As, Hg and Se compared to other foodstuffs. The highest concentrations of As, Hg and Se were found in Hijiki-algae (As: 59 mg/kg, dry), Tuna (Hg: 1.1 mg/kg, dry) and Bonito (Se: 4.5 mg/kg, dry). It is known that As exists in seaweed as an organic form, which is not toxic. Sr

concentration in seaweed was higher than the other foodstuffs.

Ratio of some elements between polished rice and brown rice was studied (see Table-3). It was observed that polished rice contains less than 50% of Mn, Mg, P, K, Rb and (Co) compared to brown rice, whereas concentrations of Zn, Cu, Br, (As) and (Cr) are only slightly lower in pollished rice. Concentrations of K, Br and Cr in rough rice were much higher than those in brown rice. In our previous paper, Cd value of 0.26 mg/kg in rice was reported (Working paper of the first RCM). The maximum permissible level of Cd in rice in Japan is 0.9 mg/kg. Since rice is the most important staple food in many asian countries, detailed studies of toxic and trace elements in rice might be important.

High Br concentrations in some rice samples (Code: Hojo) might be reflected by the high water soluble Br concentration in the soil. Because these samples were collected from rice plants cultivated in submerged field soil (not in paddy soil). This suggests that concentrations of some elements in rice may highly be influenced by the concentrations of the elements in soil, specially in the newly reclaimed (submerged) rice field.

Concentrations of Hg, Se and As in many vegetable samples were under the limits of detection. Leaf vegetable specifically spinach contained, in general, higher Zn, Fe and Mn than potatos and rice.

Table-1 Trace and major elements in foodstuffs by NAA (mg/kg, dry)

	Sample	Code	Zn	Se	As	Hg	Cr	Co	Fe	Rb	Cs	Br	K
	(a) Marine foods												
F2	Salmon	Iba87	13	-	2.1	0.1	-	0.02	15	3.1	0.11	19	15000
F5	Tuna	Iba87	11	2.2	7	1.1	-	0.01	9.1	2.1	0.13	15	14000
F6	Bonito	A-27	28	4.5	6.6	0.2	-	0.05	87	1.7	0.09	15	10500
F7	Flatfish	A-19-a	42	1.0	3.1	0.2	0.85	0.03	23	2.7	0.03	6.5	13000
F12	Oyster	Iba87	350	2.3	8.3	0.3	0.52	0.19	210	3.4	0.04	83	7600
F8	Hijiki-algae	I-63	7.6	-	59	-	0.48	0.2	62	50	0.05	560	96000
F9	Wakame-algae	I-64	10	-	23	-	0.45	0.08	75	20	0.03	320	51000
F11	Konbu-algae	A-49-a	12	-	34	-	0.57	0.13	56	17	0.05	690	42000
	(b) Rice												
D3	Rough rice	Hojo 87	32	(0.16)	-	-	0.20	0.03	24	28	0.053	12	4100
D2	Brown rice	Hojo 87	28	0.11	-	(0.04)	0.04	0.02	15	17	0.042	4.3	2600
D1	Polished rice	Hojo 87	22	0.11	-	(0.03)	0.03	0.009	-	5.1	0.014	3.9	850
D4	Brown rice	R-2	22	-	0.15	-	0.04	0.03	12	19	0.012	0.82	2700
D5	Polished rice	R-2	16	-	0.12	-	0.06	0.01	4.1	6.3	0.009	0.66	950
D6	Cooked rice	R-2	15	-		-	0.05	0.04	-	2.3	0.02	0.68	460
D7	Polished rice	Nakami 84	16	-	0.056	-	0.04	-	-	2.6	0.013	-	880
D8	Polished rice	Johok 84	15	-	0.094	-	-	-	5.2	5.3	0.040	0.50	710
A9	Polished rice	F1-9c	17	0.034	-	< 0.05	-	< 0.02		1.5			

(Table-1 continued)

	Sample	Code	Zn	Se	As	Hg	Cr	Co	Fe	Rb	Cs	Br	K
D9	Polished rice	Hojo 85	24	0.096	-	-	-	0.01	8.1	6.6	0.014	2.1	1740
D10	Polished rice	Aboke 86	17	-	0.11	-	0.06	0.007	6.6	6.8	-	0.41	1040
D11	Polished rice	T.Sawa87	16	-	0.093	-	0.04	-	3.2	1.5	-	0.86	930
F1	Polished rice	Iba 87	13	-	0.14	-	0.04	0.01	-	0.98	-	(0.2)	630
	(c) Vegetables												
E1	Yam	L-11	17	-	-	-	0.13	0.03	26	5.7	0.013	21	28000
E2	Potato	L-14	15	-	-	-	0.16	0.06	29	8.5	-	5.8	23000
F3	Sweet potato	L-13	4.2	-	-	-	0.11	0.05	14	14	0.026	10	11000
E3	Welsh onion	L-24-a	45	-	-	-	0.19	0.03	29	4.7	-	8.8	28000
E4	Cucumber	L-8	92	-	-	-	-	0.08	107	16	-	68	65000
E5	Carrot	A-41-a	33	-	-	-	0.13	0.03	47	78	0.14	3.8	41000
E6	Chinese Cabbage	L-2	48	-	-	-	-	0.08	74	27	0.017	18	44000
E7	Burdock	L-15	-	-	-	-	-	0.10	-	-	-	30	24000
E8	Cabbage	L-9	64	-	-	-	-	-	98	54	0.093	9.4	63000
E9	Shitake-Mushroom	L-5	62	-	0.14	0.1	0.31	0.16	82	128	0.26	3.1	30000
A5	Cabbage	F1-5c	24	<0.1		<0.05	0.15	0.05	45	25	0.03		
A6	Sweet potato	F1-6c	3.8	<0.1		<0.05	0.09	0.03	14	9.1	0.01		

Table 2 Trace and major elements in foodstuffs by ICP (mg/kg, dry)

	Sample	Code	Zn	Cu	Fe	Mn	Ba	Sr	Mg	Ca	P	K
	(a) Marine foods											
27	Flatfish	A-19-b	40	6.3	17	1.7	1.7	1.9	990	650	7010	12500
28	Shirasu	A-43-a	52	8.5	22	4.1	(0.6)	24	2250	5850	11000	6380
59	Salmon	Iba 87	14	(2.9)	13	(0.8)	(0.6)	(0.8)	1160	520	9240	16040
60	Tuna	Iba 87	13	1.7	10	(0.7)	(0.54)	<0.8	1290	120	8750	14800
61	Oyster	Iba 87	350	34	280	29	(3.1)	6.6	1580	720	7000	7200
33	Wakame-algae	A-47-a	35	5.7	76	5.8	11	350	4150	6400	3400	2510
34	Hijiki-algae	A-45-a	19	13	66	31	17	690	6170	12900	1230	44000
	(b) Rice											
4	Polished rice	Nakami84	19	6.0	5.5	18	<0.4	<0.2	350	170	1160	1230
8	Polished rice	Hojo 85	25	3.1	5.9	11	<0.3	<0.2	260	87	960	1620
9	Polished rice	Aboke 86	18	2.7	5.6	12	<0.2	<0.2	470	77	1150	1060
10	Polished rice	T.Sawa87	18	2.1	4.3	8.7	<0.2	<0.2	360	68	1170	910
11	Polished rice	Nakama83	15	2.4	3.9	12	<0.2	<0.2	340	68	1150	885
12	Brown rice	Nakama83	22	2.6	8.4	32	<0.3	<0.2	1290	120	3390	2640
13	Polished rice	R2-83	17	1.9	4.6	14	<0.2	<0.2	360	73	1200	890
14	Brown rice	R2-83	24	2.2	11	36	<0.4	<0.2	1130	120	3070	2500
54	Polished rice	R-1 83	18	1.5	7.0	8.2	<0.2	<0.2	470	70	1350	990
55	Brown rice	R-1 83	24	1.8	11	17	1	<0.3	1150	110	2860	2310
57	Cooked rice	R-2 83	16	2.0	7.2	5.3		0.8	120	100	680	460

(Table-2 continued)

	Sample	Code	Zn	Cu	Fe	Mn	Ba	Sr	Mg	Ca	P	K
	(c) Vegetables											
15	Spinach	A-50-a	72	15	160	86	1.6	19	7360	10700	6080	67600
16	Carrot	A-41-a	40	17	55	24	25	23	2180	5180	4780	50800
17	Welsh onion	L-24-a	53	8.8	34	11	5.9	16	1740	3170	5140	26600
18	Lettuce	L-27	57	11	72	25	1.3	6.6	1820	3470	5660	40200
19	Shitake	L-5	70	18	79	27	1.1	1.5	1460	480	5840	29000
20	Radish	L-6	44	9.6	54	7.8	2.2	12	1540	3500	5660	37800
21	Cucumber	L-8	110	24	98	39	9.9	24	4570	8020	12500	68500
22	Cabbage	L-9	76	15	88	39	5.3	29	2550	11700	10100	63700
23	Corn	L-t-4	54	9.4	28	19	2.3	1.2	1660	320	4350	12700
24	Burdock	L-t-7	31	13	23	2.9	4.1	22	2660	2080	2040	15100
25	Pumpkin	L-t-8	48	11	48	24	7.0	21	2360	5220	4890	35900
30	Spinach	L-t-17a	98	13	150	80	5.5	34	10400	12150	5800	66000
35	Eggplant	L-t-2	28	11	32	25	1.7	8.2	2140	1820	3240	38200
36	Cucumber	L-t-5	70	15	65	23	5.2	40	4490	8200	9850	67000
37	Carrot	L-t-1a	53	13	80	19	25	31	2090	3630	5950	60600
38	Green pepper	L-t-11	42	14	61	19	1.9	4.7	2150	910	4100	37500
39	Ginger	L-t-13a	43	9.6	51	16	8.2	69	2310	12300	5960	49900
40	Chinese cabbage	L-t-18	46	9.5	46	240	15	12	2870	1960	2620	27000
41	Taro	L-t-9a	65	12	37	58	16	55	1790	8250	2640	35100
42	Sweet potato	L-t-10	7.1	4	17	13	1.2	4.7	780	980	1070	11900
43	Yam	L-11	20	8.6	23	3.0	2.4	3.4	980	1020	2550	26700
44	Potato	L-14	16	6.2	26	6.1	2.1	1.5	930	390	2560	21200
45	Chinese cabbage	L-2	58	9.0	66	27	7.3	16	2620	7670	8240	45000
46	Radish	L-t-21a	32	7.6	41	6.7	6.1	20	1770	3500	4990	44100
47	Shungiku	L-18a	44	11	88	84	9.5	31	2810	12500	2870	60600
48	Tomato	L-23	31	13	52	13	0.5	1	1660	1410	3860	37300

Table-3 Ratio of some elements between polished rice and brown rice.

(a) NAA

			ZN	SE	AS	CR	CO	FE	RB	CS	BR	K
HOJ087	ROUGH RICE	ppm	32	0.16		0.2	0.03	24	28	0.053	12	4100
	BROWN RICE	ppm	28	0.11		0.04	0.02	15	17	0.042	4.3	2600
	POLISH.RICE	ppm	22	0.11		0.03	0.009		5.1	0.014	3.9	850
	POL./BRA.		0.79	1.00		0.75	0.45		0.30	0.33	0.91	0.33
R-2	BROWN RICE	ppm	22		0.15	0.04	0.03	12	19	0.012	0.82	2700
	POLISH.RICE	ppm	16		0.12	0.06	0.01	4.1	6.3	0.009	0.66	950
	COOK.RICE	ppm	15			0.05	0.04		2.3	0.02	0.63	460
	POL./BRA.		0.73		0.80	1.50	0.33	0.34	0.33	0.75	0.80	0.35
Average	POL./BRA.		0.76			1.13	0.39		0.32	0.54	0.86	0.34

(b) ICP-AES

			ZN	CU	FE	MN	BA	SR	MG	CA	P	K
NAKAMA83	BROWN RICE	ppm	22	2.6	8.4	32	<0.3	<0.2	1290	120	3390	2640
	POLISH.RICE	ppm	15	2.4	3.9	12	<0.2	<0.2	340	68	1150	885
	POL./BRA.		0.68	0.92	0.46	0.38	(0.67)	(1.00)	0.26	0.57	0.34	0.34
R-2	BROWN RICE	ppm	24	2.2	11	36	<0.4	<0.2	1130	120	3070	2500
	POLISH.RICE	ppm	17	1.9	4.6	14	<0.2	<0.2	360	73	1200	890
	COOK.RICE	ppm	16	2	7.2	5.3		0.8	120	100	680	460
	POL./BRA.		0.71	0.86	0.42	0.39	(0.50)	(1.00)	0.32	0.61	0.39	0.36
R-1	BROWN RICE	ppm	24	1.8	11	17	1	<0.3	1150	110	2860	2310
	POLISH.RICE	ppm	18	1.5	7	8.2	<0.2	<0.2	470	70	1350	990
	POL./BRA.		0.75	0.83	0.64	0.48	(0.20)	(0.67)	0.41	0.64	0.47	0.43
Average	POL./BRA.		0.71	0.87	0.51	0.42	(0.46)	(0.89)	0.33	0.60	0.40	0.37