Short Communication

Dietary Intakes of Copper, Iron, Manganese, and Zinc for Ukrainians

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Abstract

Daily intakes of four essential trace elements (Cu, Fe, Mn, and Zn) in Ukrainian subjects were estimated in relation to the health effects on habitants after the Chernobyl accident. Two hundred and sixty-eight diet samples were collected from twenty-five oblasts (regions) using a duplicate portion method. The elements were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). For Ukrainians, median daily intakes of Cu, Fe, Mn, and Zn were 0.695, 7.87, 2.28, and 6.57 mg per person, respectively. The intakes of Cu, Fe, Mn, and Zn in Ukrainians were approximately two times lower than worldwide reported values.

Keywords : copper, iron, manganese, zinc, dietary intake, Ukrainian, Chernobyl accident

Introduction

In April 1986, global contamination by radioactive nuclides was caused by the Chernobyl accident. Contamination in the environment has been studied during the years since then the accident [1]. We have made several studies in the Ukraine, from the viewpoints of radiation protection, nutrition and public health [2-5]. In such studies, the relationship of radioactive and non-radioactive nuclides in food chains is important for understanding their environmental behaviors. Therefore, it is necessary to collect information on dietary mineral intake to quantify the background level in Ukrainian subjects. Furthermore, to know a dietary intake of essential trace elements, which occurs largely in the form of organic complexes and functions as enzymes, is important to keep habitants' health from the nutritional viewpoints. However, data on the dietary element intakes for Ukrainians are not well documented.

In the previous reports [6-8], dietary intakes both of radioactive and non-radioactive nuclides for Ukrainians living areas contaminated by the Chernobyl accident were described. In this paper, a dietary intake of four essential trace elements (Cu, Fe, Mn, and Zn) in whole Ukraine was estimated and also compared the intakes between the contaminated and non-contaminated areas.

Materials and Methods

Materials

Two hundred and sixty-eight diet samples were collected from twenty-five blasts of Ukraine shown in Fig. 1. At least five samples were collected from one oblast by a duplicate portion method during 1997 and 2005. Each sample consisted of the total daily whole meals collected for children or adult males. Drinking water was not included in the samples. Five samples were also collected in Japanese adult males in Mito, Japan during 1990. The samples were homogenized, freeze-dried and kept in a sample bottle before elemental analyses. For ICP-AES,

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Fig. 1 A map of twenty five oblasts in Ukraine.

stock solutions (1,000 ppm) of Cu, Fe, Mn, Zn, and Y were prepared from a standard material (Specture, Spex Industries, Edison, NJ). Ultra-pure acids (nitric acid, perchloric acid and hydrofluoric acid, Tamapure [AA-100, Tama Chemical Co. Tokyo) were used. Standard reference materials, e.g. NIST SRM 1548a (Typical diet), 1571 (Orchard leaves), 1575 (Pine needles), and 1577a (Bovine Liver) were purchased from National Institute of Standards and Technology, Gaithersburg, MD.

Analyses of whole diet samples

The analytical procedure employed has been described in detail elsewhere [9] ; only a summary is given in this section. Approximately one gram of freeze-dried sample was digested with a mixture of nitric acid (5-10 cm^3), perchloric acid (0.5 cm^3), and hydrofluoric acid (0.5 cm^3) in a 100 cm^3 Teflon vessel using a microwave digestion system, MLS MEGA1200 (Milestone s.r.l. Bergamo, Italy). The acid digestion and subsequent sample preparation procedure were carried out in a clean-air hood (Class 100) installed in a clean room (Class 5,000). The ICP-AES instrument used was a Thermo Jarrell Ash Model ICP-AES Model IRIS AP (Franklin, MA). Yttrium was used as an internal standard. Specifications of the instrument and the operating conditions employed have been also described elsewhere [9].

Results and Discussion

The analytical procedure was checked by using standard materials, NIST SRM 1548a, 1571, 1575, and 1577 a. Accuracies of the elements were good, i.e. errors were within ±8% in comparison to the certified or informative values. Detection limits ($\mu g\ dm^{-3}$) are as follows : Cu (0.62) ; Fe (0.10) ; Mn (0.031) ; and Zn (0.16).

Concentrations and dietary intakes of trace elements in Ukrainians

Ukrainian samples consisted of seven child diet samples and two hundred and sixty-one adult diet samples. A combined samples was treated as the Ukrainians because the number of child samples (n=7) was small. For Ukrainian samples, distributions of both concentrations (on dry-weight basis) and daily intakes for all elements were spread out on the right side. Cupper concentration and zinc intake were not a significantly normal distribution ($p<0.01$) due to their skewing and kurtosis. Ranges of concentrations (n=268) were as follows : Cu 0.574-6.69 ; Fe 7.75-146 ; Mn 2.03-30.9 ; and Zn 6.64-70.4 μg /g-dry. Copper, Mn, and Zn were found to be a narrow ranges under 15-folds. The iron was a high range of 19-fold. Median and geometric mean (in parentheses) concentrations of the elements (μg/g-dry) were as follows : Cu 2.16 (2.18) ; Fe 23.9 (24.9) ; Mn 6.75 (6.95) ; and Zn 19.5 (19.4). The daily intakes of twenty five oblasts in Ukrainians are shown in Table 1. The intakes of Cu, Fe, Mn, and Zn showed a wide range of 40-80-fold differences between minimum and maximum values. Median and geometric mean (in parentheses) of daily intakes per person (n=268) are as follows : Cu 0.695 (0.708)mg ; Fe 7.89 (8.09)mg ; Mn 2.28(2.26) mg ; Zn 6.57 (6.29)mg. Correlations of the mineral intakes were also checked. High correlation factors (r) were found between the following pairs of : Cu-Fe 0.569, Cu-Mn 0.536, Cu-Zn 0.496, Fe-Zn 0.458, Fe-Mn 0.392,

Table 1 Daily intakes of Cu, Fe, Mn, and Zn in 25 Ukrainian oblasts.

Capital of oblast	Daily intake (mg per person)								n**
	Cu		Fe		Mn		Zn		
	Median	GM*	Median	GM*	Median	GM*	Median	GM*	
Cherkassy	0.524	0.545	7.61	7.72	2.17	2.24	5.10	5.23	6
Kiev	0.661	0.681	6.75	6.80	1.86	2.08	6.39	6.28	12
Kirovograd	0.619	0.654	8.74	8.00	2.17	2.17	6.66	6.99	6
Poltava	0.563	0.657	8.20	8.28	2.12	2.22	7.33	6.85	6
Vinnitsa	0.616	0.697	6.17	5.97	2.17	2.31	4.51	4.38	6
Dnepropetrovsk	0.668	0.636	9.43	8.61	2.37	2.38	6.65	7.35	6
Donetsk	1.14	1.02	7.75	8.23	2.48	2.39	8.42	8.03	6
Kharkiv	0.631	0.646	6.52	7.50	2.19	2.27	7.00	7.07	6
Lugansk	0.639	0.654	6.73	7.07	2.04	1.93	6.45	6.33	6
Chernigov	0.592	0.637	8.65	8.87	1.98	1.89	3.88	4.15	6
Sumy	0.605	0.621	7.19	7.88	1.93	1.85	8.80	9.61	6
Kherson	0.669	0.656	6.48	7.02	2.12	2.30	6.94	6.70	6
Nikolayev	0.750	0.919	8.47	9.09	2.82	2.62	8.97	8.99	7
Odessa	1.14	1.08	9.70	10.7	2.10	2.20	11.4	9.99	6
Simferopol	0.956	0.998	9.04	9.31	2.09	3.06	8.52	8.60	5
Zaporozhye	0.935	0.873	8.77	8.81	1.97	1.99	10.1	10.1	6
Chernovtsy	0.621	0.716	8.59	8.43	2.05	1.80	8.11	8.64	6
Ivano-Frankovsk	0.570	0.619	6.86	6.85	1.77	1.84	5.36	5.12	6
Khmelnitskiy	0.594	0.558	6.26	7.26	1.82	2.10	7.09	7.19	6
Volyn	0.531	0.582	6.38	6.51	1.70	2.07	6.37	6.64	6
Lvov	0.907	0.874	7.89	9.05	2.81	2.77	6.97	7.21	6
Rivno	0.611	0.652	7.45	8.62	2.26	2.19	5.30	5.86	30
Ternopol	1.11	1.20	12.3	13.5	2.67	2.89	8.95	8.43	6
Transkarpatia	0.592	0.549	5.06	4.85	1.80	1.49	3.78	4.53	5
Zhitimir	0.759	0.707	8.15	8.21	2.56	2.40	5.64	5.57	95
Overall	0.695	0.708	7.87	8.09	2.28	2.26	6.57	6.29	268
Japan	1.36	1.29	7.49	7.67	4.72	4.62	9.39	8.67	5

*Geometric mean. **Number of samples

Zn-Mn 0.349 ($p<0.001$). There are possibilities that these pair elements behave in the same manner in the food chain. Collecting those relationships in diets should be a basis for comparison in future work on nutrition and health studies.

Comparison of the intakes between contaminated and non-contaminated areas by the Chernobyl accident

These four elements are known as essential trace elements and have an important role in human health maintenance. The twenty five regions of Ukraine were divided into two areas depending on intakes of ^{137}Cs of each region. Three oblasts of higher daily ^{137}Cs intakes per person, e.g. Rivno 571 Bq, Zhitimir 117 Bq, and Kiev 88.8 Bq, were categorized into a contaminated area. The rest of twenty-two regions, which were under 22 Bq were categorized into a non-contaminated area. Number of samples collected in the contaminated and non-contaminated areas was one hundred and thirty-seven and one hundred and thirty-one, respectively. Daily mineral intakes between the two areas were compared. Results are shown in Table 2. There are no statistically difference in the intakes of Cu, Fe and Mn. Only for Zn, there was a statistically significant difference ($p<0.01$) in a non-parametric test (Mann-Whitney test). The reason is unclear now, however, a geological difference would be one of the specious reasons ; the north and northwest of Ukraine is called the Pripyat Marshes consisting of lots of swamps and gray podzol soils. It is known as less adaptable soils to agriculture. Behavior of some elements in food chains would be different from that of fertile chernozem soils of the southern area. Daily Zn intakes of the three contaminated oblasts were also statistically different with those of several oblasts in southern Ukraine, e. g., Summy, Nikolayev, Odessa, and Zaporozhye.

Comparison of present results with world values

Results of Ukrainians and Japanese are summarized in Table 3. Comparing with the reported values [10], Ukrainian intakes were lower than those of Japanese in all elements. However, Ukrainian intakes were lower than Japanese except Fe due to the small analyzed sample numbers (n=5) in this study. Furthermore, Ukrainian intakes were compared with worldwide reported values [11], and Reference Man [12], which is equivalent to Europeans and North Americans. The intakes of four ele-

Table 2 Comparison of Ukrainian mineral intakes between contaminated and non-contaminated areas by the Chernobyl accident

Element	Unit*	Area**	Range min	Range max	Median	Geometric mean	Arithmetic Mean ± SD	No#
Cu	mg	Contaminated	0.084	2.60	0.713	0.692	0.826 ±0.501	137
		Non-contaminated.	0.288	4.13	0.671	0.725	0.803 ±0.445	131
		Overall	0.084	4.13	0.695	0.708	0.814 ±0.474	268
Fe	mg	Contaminated	1.09	56.3	7.65	8.16	10.1 ±7.9	137
		Non-contaminated.	2.86	58.9	7.91	8.02	8.79 ±5.41	131
		Overall	1.09	58.9	7.87	8.09	9.46 ±6.77	268
Mn	mg	Contaminated	0.18	15.0	2.44	2.33	2.94 ±2.43	137
		Non-contaminated.	0.672	7.96	2.18	2.19	2.40 ±1.11	131
		Overall	0.18	15.0	2.28	2.26	2.67 ±1.91	268
Zn$	mg	Contaminated	0.431	18.3	5.61	5.69	6.48 ±3.33	137
		Non-contaminated	2.62	22.8	6.83	6.99	7.57 ±3.17	131
		Overall	0.431	22.8	6.57	6.29	7.02 ±3.29	268

*Daily intake mg per person.
**Contaminated and non-contaminated (lower contaminated) areas of Ukrainian territory by the Chernobyl accident
#Number of sample
$Significantly statistic different, p<0.01 between contaminated and non-contaminated areas

Table 3 Comparison of daily mineral intakes of Ukrainians and reported data*

Element	Present results		Literature				
	Ukrainian (Median)	Japanese (Median)	Japanese**		World value***		RM#
			Mean	Range	Median	Range	
Cu	0.695	1.36	1.5	0.76-3.6	1.5	1.0-2.8	3.5
Fe	7.87	4.49	10	3.9-17	13	5.1-47	16
Mn	2.28	4.71	3.8	2.7-9.4	3.1	2.2-8.8	3.7
Zn$	6.57	9.38	9.1	4.3-30	10	4.2-19	13

*Daily intake mg per person. **K. Shiraishi (1994) [10]. #R.M. Parr (1992) [11].
$Reference Man (ICRP 1975) [12].

ments in Ukrainians were approximately two times lower than the two representative reported values.

Conclusion

The intakes of four essential trace elements, Cu, Fe, Mn and Zn in Ukrainians were found to be 0.695 mg, 7.87 mg, 2.28 mg, and 6.57 mg, respectively. The element intakes of Ukrainian subjects were lower than the reported values. Ukrainian Zn intakes in the contaminated areas by the Chernobyl accident were different from the non-contaminated areas

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