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Letter to Editor

Safety of Fresh Fruits and Juices Available on the Polish Market as Determined by Heavy Metal Residues

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Abstract

The content of Pb, Cd, Cu and Zn in fresh fruit and juices was determined using atomic absorption spectrometry (AAS) to determine the safety of some food available in the Polish market. It was found that most fruit samples (90.4%) contained low levels of heavy metals. However, the remaining 9.6% had increased heavy metal contents (Pb 2.2%, Cd 4.4%, Cu, 1.5%, Zn 1.5%). Most fruit juice sample (88%) met the national standard criteria, but 12% exceeded the permissible limits for Pb and Cd (3% and 9%, respectively).

The results contained in this paper were presented in the 14th IGWT Symposium, Beijing, China, August 23-29, 2004.

Keywords: fruits, juices, lead, cadmium, copper, zinc

Introduction

It is widely accepted that a diet rich in fruits that are good sources of vitamin C, carotenoids, minerals (especially Mg, K) and various kinds of antioxidants and dietary fibre (pectin) is protective against degenerative and chronic diseases such as cancer and cardiovascular diseases [1, 2]. Some of these functional compounds remain after processing and are present also in fruit products, including juices. For these reasons recent dietary guidelines have recommended high fruit product consumption. The beneficial health effects of fruits and their products depends on the amount consumed in a daily diet, type of fruit and the content of biologically active compounds. On the other hand, the quality of fruit products is diminished with increasing concentration of toxic compounds, environmental pollutants (especially pesticides), polychlorinated biphenols (PCB's) and heavy metals, especially Pb and Cd. The main source of human exposure to Pb and Cd is food, which is believed to provide about 80-90% of daily doses [3, 4]. Pb and Cd toxicity is well documented and is recognized as a major environmental health risk throughout the world. Pb affects humans and animals of all ages, but the affects of lead are most serious in young children. Cadmium is a toxic and carcinogenic element. The International Agency for Research on Cancer has identified Cd as a known human carcinogen [4]. Pb and Cd poisoning results from the interaction of the metal with biological electron-donor groups, such as the sulfhydryl groups, which interferes with a multitude of enzymatic processes. Clinical manifestations of Pb toxicity include symptoms referable to the central nervous system, the peripheral nervous system, the hematopoietic system, the renal system, and the gastrointestinal systems. Cd is a cumulative nephrotoxicant that is absorbed into the body from dietary sources and cigarette smoking [4]. The con-

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tent of heavy metals in various food products available in Poland has been a subject of numerous studies throughout the last decades [5-10]

The aim of the present study was to evaluate the safety of selected fresh fruits and fruit juices available in Poland in the region of Wielkopolska (Western Poland) during 1993-1998, as determined by the content of Pb, Cd, Cu and Zn.

Material and Methods

Various kinds of fresh fruits (136 samples) and fruit juices (66 samples) were randomly collected according to the official procedure from producers and from the market by the Officers of the Sanitary and Epidemiology Station for region of Poznań, Kalisz and Ostrów Wielkopolski and submitted to a laboratory for analysis.

The content of metals in fruit and juice samples was determined according to a procedure advised by the National Institute of Hygiene [11]. The fruit samples were cleaned, peeled (if necessary) and washed to obtain edible parts prior to analysis, then homogenized. Samples were weighed (10-50 g) in quartz crucibles, dried at 105°C for 24 hours and subsequently ashed in a muffle furnace at 400°C. The juice samples (100 ml) were poured into quartz crucibles and evaporated to dry residue at 100°C, then ashed in a muffle furnace like the fruit samples. Ash was dissolved in 1mol/l nitric acid (GR, ISO, Merck) and filled up in 50 ml volumetric flasks to the mark by the same acid. The content of Pb and Cd in the mineralised sample was determined after extraction of the complexes with APDC (1-pyrrolidindithiocarbamate ammonium) to MIBK (methyl-*iso*-buthylketon) phase (GR, ISO, Merck) using the flame atomic absorption spectrometry (F-AAS) method. The content of Zn and Cu in the diluted sample solutions was determined by the same method (spectrometer AAS-3, Zeiss with BC). All the instrumental conditions applied for metal determinations were set in accordance to the general recommendations (wavelengths for Pb, Cd, Zn and Cu: 283.3 nm, 228.8 nm, 213.9 nm and 324.8 nm, respectively) [12].

The accuracy and precision of the method was assured by simultaneous analysis of the reference material (lyophilized vegetable sample) provided by the National Institute of Hygiene, Warsaw, Poland. The laboratory obtained acceptable recovery for the analyzed metals (z-score values in accepted limits). The results were expressed in mg/kg fresh weight and evaluated by comparison with the Maximum Permissible Limits (MPL) on the basis of the National Food Standards [13]. Descriptive statistical parameters (mean, median, range) were calculated using Excel software (ver. 6).

Results

The mean, median, and range values for the content of Pb, Cd, Zn and Cu in fruits and fruit juices are present-

Table 1. The mean, median and range values for Pb, Cd, Cu and Zn contents of selected fruits.

Fruit type (n)	Parameter	Pb (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Zn (mg/kg)
	MPL	0.3	0.04	4.0	10.0
Strawberries (24)	mean	0.074	0.021	0.816	3.431
	median	**0.054**	**0.011**	**0.577**	**2.355**
	range	0.017-0.337	0.000-0.130	0.229-4.74	1.00-13.30
	% >MPL	**4**	**12**	**4**	**4**
Cherries (24)	mean	0.059	0.007	0.881	1.492
	median	**0.061**	**0.006**	**0.680**	**1.200**
	range	0.012-0.141	0.001-0.036	0.250-3.500	0.600-2.877
	% >MPL	0	0	0	0
Black currant (24)	mean	0.084	0.007	0.695	3.179
	median	**0.073**	**0.007**	**0.718**	**3.030**
	range	0.004-0.280	0.002-0.019	0.097-7.070	1.340-4.660
	% >MPL	0	0	**4**	0
Pears (24)	mean	0.042	0.006	1.062	2.059
	median	**0.044**	**0.004**	**0.960**	**1.300**
	range	0.008-0.089	0.001-0.058	0.300-2.310	0.410-17.30
	% > MPL	0	**4**	0	**4**
Apples (40)	mean	0.078	0.009	0.607	1.723
	median	**0.068**	**0.006**	**0.414**	**1.185**
	range	0.007-0.320	0.000-0.046	0.100-1.920	0.000-4.460
	% > MPL	**4**	**4**	0	0

Symbols: MPL – maximum permissible levels for elements as established by the National Ministry of Health, n – number of samples studied (given in parenthesis)

ed in Tables 1 and 2. The contents of Pb (mean and median levels) of fruits grown in non-polluted regions were relatively low and did not exceed MPL (0.3 mg/kg fresh weight); however, 3 out of 136 samples (2.2%) had increased Pb levels (1 strawberry and 2 apple samples). The highest content of Pb was found in black currant (0.073 mg/kg) and the lowest in pears (0.044 mg/kg). Similar Pb levels of fruit samples were detected by Wojciechowska-Mazurek et al. [5]. The contents of Cd of fruits (mean and median values) were also low, comparable with the data reported by other authors [6], and did not reach the MPL (0.04 mg/kg). Nevertheless, 6 out of 136 samples (4.4%) had high Cd content (3 strawberry, 1 pear and 2 apple samples).

Results of the monitoring studies carried out in Poland in 2000 showed that the mean Pb content of strawberries was regionally dependent [7]. The lowest Pb level in strawberries (0.03 mg/kg) was found in the Central part of the country, higher in northeastern Poland (0.06 mg/kg) while the highest was determined in the southern region of Poland – 0.20 mg/kg. Generally, 6.4% of 423 analyzed strawberry samples had elevated Pb levels (above the MPL). On the other hand, the mean Pb content of apples was lower, 0.02-0.03 mg/kg independent of the region. None of the 309 analyzed apple samples exceeded the MPL for this metal. Concerning the fruit Cd content monitoring data, the mean level of this toxic metal in strawberries was similar in all three regions of Poland, ranging from 0.018 to 0.023 mg/kg, while in apples it was much lower, 0.003-0.005 mg/kg. Relatively high percentage of strawberries (13.7%) had increased Cd content, whereas no single apple sample exceeded the MPL for Cd [5]. The differences in the concentrations of Pb and Cd in various fruit types growing in the same environmental conditions indicate specific affinity to accumulate these metals. Generally speaking, 6.6% of all analyzed fruit samples in this study had increased Pb and Cd levels, which is comparable with the data obtained for other regions of the country [5, 6, 8, 9] and in some European countries [14]. These toxic metals in fruit may originate from various sources, basically from environmental (dust fallout, soil). According to the national monitoring survey [5], the average Polish diet in the year 2000 provided approximately 0.134 kg fruit/day (budgetary data). The estimated average daily dietary Pb and Cd content was 0.0964 and 0.0234 mg, respectively, which equals 45% and 39% of ADI for these toxic metals. Fruit was calculated to provide 0.0067 mg Pb/day and 0.0008 mg Cd/day in the average daily diet that stands for 7% and 3.4% of ADI for Pb and Cd.

In the case of the essential elements such as Cu and Zn, their mean and median values were safe – far below the MPL. The highest median Cu content was found in pears (0.960 mg/kg) while the lowest was in apples (0.414 mg/kg). Only 2 samples had increased Cu content (1 strawberry, 1 black currant), which may originate with Cu-containing pesticides used in plant protection.

The content of Zn of fruit was relatively low and did not pose a toxicity risk. The highest median Zn content

Table 2. The mean, median and range values for Pb, Cd, Cu and Zn contents of juices.

Juice type (n)	Parameter	Pb (mg/l)	Cd (mg/l)	Cu (mg/l)	Zn (mg/l)
	MPL	0.3	0.03	3.5	5.0
Orange juice (10)	mean	0.125	0.015	0.486	1.309
	median	**0.095**	**0.010**	**0.245**	**1.177**
	range	0.046-0.251	0.004-0.040	0.047-1.750	0.063-2.830
	% > MPL	0	**10**	0	0
Grapefruite juice (10)	mean	0.116	0.010	0.559	1.513
	median	**0.109**	**0.009**	**0.250**	**1.155**
	range	0.047-0.238	0.005-0.016	0.106-1.560	0.260-3.390
	% > MPL	0	0	0	0
Aronia juice (11)	mean	0.140	0.016	0.550	1.144
	median	**0.110**	**0.016**	**0.420**	**0.850**
	range	0.020-0.430	0.006-0.043	0.110-1.830	0.310-1.958
	% > MPL	**9**	**9**	0	
Apple juice (11)	mean	0.169	0.017	0.351	0.937
	median	**0.130**	**0.016**	**0.283**	**0.550**
	range	0.051-0.460	0.005-0.060	0.106-0.820	0.242-2.440
	% > MPL	**9**	**9**	0	0
Black currant juice (24)	mean	0.135	0.021	0.626	1.648
	median	**0.110**	**0.017**	**0.370**	**1.254**
	range	0.063-0.260	0.010-0.049	0.240-1.840	0.360-3.170
	% > MPL	0	**12**	0	0

Symbols are the same as those used in Table 1.

was detected in black currants (3.03 mg/kg) while the lowest was in cherries (1.2 mg/kg). Only 2 samples (1.5% of all, namely 1 strawberry and 1 pear) exceeded the MPL from Zn (10.0 mg/kg). It was found that 9.6% of all the studied fruit samples had increased heavy metal levels. Results of fruit heavy metal content monitoring in 2000 [5] showed that 6.7% of strawberry samples had elevated Zn content, while none for Cu content. Similar results concerning heavy metal contents were reported by other authors in Poland. Zalewski et al. [8] analyzed the content of Fe, Mn, Ni, Pb, Cu, Zn and Cd in 229 vegetables and fruit samples grown in the province of Siedlce. It was found that 49 (21%) and 4 (1.7%) studied samples exceeded the limit for Cd and Pb, respectively. Wojciechowska-Mazurek et al. [9] determined the content of Pb, Cd, Hg, Zn and Cu in various species of fruit gathered in Poland in 1989-1991. The highest Pb levels were found in strawberries, raspberries and currants (about 0.1 mg/kg on average), Cd in raspberries and strawberries (mean 0.02 mg/kg). The levels of all these metals were lowest in apples and pears (Pb mean 0.010-0.089 mg/kg, Cd mean 0.001-0.006 mg/kg, Cd mean 0.001-0.006 mg/kg). The Hg, Zn and Cu levels were generally low. On the other hand, the content of metals in fruit grown in highly industrialized areas was significantly higher compared to the rural regions. The monitoring study performed by Szymczak et al. [10] on the content of Pb and Cd in vegetables, fruits, and cereals showed that Pb content ranged from 0.013 to 0.144 m/kg and Cd from 0 to 0.042 mg/kg. Tahvonen and Kumpulainen [14] determined the contribution of vegetables and berries to the intake of Pb and Cd in Finland with major vegetable groups as well as strawberries and black currants. The mean Pb and Cd contents found were: 0.005 and 0.031 μg/kg (imported), strawberry 0.007 and 0.014 mg/kg, black currant 0.013 and 0.001 mg/kg. The contents found in their study were the lowest reported so far in Finland and equal to or lower than those found elsewhere.

The contents of Pb and Cd of fruit juices were low and conformed to the national standards. However, 2 samples had increased Pb levels (> 0.3 mg/l, namely 1 aronia and apple juice), while 6 samples out of 66 (9%) exceeded the MPL for Cd (0.03 mg/l, 1 of orange, aronia, apple and 3 of black currant juice samples). Generally, 8 out of 66 (12% of samples) did not meet the safety standards concerning the level of toxic metals, which is a relatively high rate. Most probably these metals may come both from fruit material as well as from technological processes (hidden source of contamination) that calls for urgent consideration (eg. application of the hazard analysis critical control points system).

The content of Cu and Zn in all the fruit juice samples were relatively low and conformed to the national standards. The highest level of Cu was found in aronia juice (0.420 mg/l) while the lowest in orange juice (0.245 mg/l). The highest level of Zn was found in black currant juice (1.254 mg/l) and the lowest in apple juice (0.550 mg/l). Generally speaking, the content of heavy metals found in fruit and fruit juices was relatively low, with only a small percentage of samples exceeding the safety standards.

Conclusions

In conclusion, we can state that most of the analyzed fresh fruit and juices samples (90.4%) taken from the Polish market are safe since the levels of Pb, Cd, Cu and Zn were below the maximum permissible level for a given element as established by the National Ministry of Health. It should be noted, however, that in the case of 2.2%, 4.4%, 1.5% and 1.5% of samples the concentration of a particular heavy metal was found to be above the MPL value for Pb, Cd, Cu and Zn, respectively.

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