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Review

Evaluation of plant products from the Legnicko–Głogowski region for their contamination with arsenic

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Abstract

Contents of arsenic were determined in plant products originating from the region of two copperworks, Głogów and Legnica. Analyses were carried out by means of atomic absorption spectrometry, using an MHS-10 unit for hydride generation (acetylene/argon), after wet mineralisation of samples.

The maximum permissible level of arsenic was not exceeded in any of the examined samples of cereals, potatoes, carrots, beetroots, cabbages, tomatoes, apples and pears, originating from the regions under scrutiny.
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Keywords: Plant products; Arsenic; AAS

Contents

1. Introduction

Arsenic is an element widely distributed in the environment. In nature, it occurs mainly in the form of sulfides, in ores of such metals as silver, lead, copper, nickel, antimony and iron. Trace amounts of arsenic are found in soil and other environmental constituents (Bieniek & Sałacki, 1996; Grajeta, 1987).

The main absorption routes of inorganic compounds of arsenic are the lungs and gastrointestinal tract. Arsenates and arsenites are absorbed from the gastrointestinal tract with a high efficiency, reaching 55–95%, while the absorption efficiency of organic compounds of arsenic from the gastrointestinal tract is 75–85% (Grajeta, 1987; Piotrowski, 2006; Tong, Von Schimding, & Prapamontol, 2000).

The highest levels of arsenic are in fish. However, the main source of heavy metals in the diet are products of plant origin (cereals, potatoes, vegetables and fruit) which

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constitute ca. 50–55% of daily food consumption (Bieniek & Sałacki, 1996; Rocznik GUS, 2004).

Both the organic and inorganic compounds of arsenic are highly toxic. In humans, most intoxications are linked with occupational exposure to the action of inorganic arsenic as well as its oxides and acids.

Nowadays, acute intoxications with arsenic compounds are sparse. They lead to functional impairment and morphological changes of stomach and intestines, and induce nausea, vomiting and diarrhoea. Compounds of arsenic may also be causative agents in the development of some neoplasms (of lungs, skin and liver). In addition, their excessive single intake induces dementia and hallucinations (Piotrowski, 2006). Exposure of a human organism to arsenic compounds is also the likely reason of disturbances in reproductive capacity of both sexes. Arsenic results in a decrease in the mass of sexual organs and the occurrence of inflammation in tissues (Concha, Vogler, Lezcano, Nermell, & Vahter, 1998).

The most susceptible to the action of arsenic compounds are children. Compared to adults, they drink more fluids, consume greater quantities of food, relative to their body mass, skin surface area and size of internal organs. What is more, children tend to put some objects into their mouth, which is an additional source of arsenic uptake (Tsuji, Benson, Schoof, & Hook, 2004).

The worldwide advance in the copper industry during the 1960s and 1970s has led to unfavourable changes in the environment. High dust emission, polluted metallurgic sewage and mine water wastes have led to air, soil and water contamination with heavy metals (Bieniek & Sałacki, 1996). Later modernisation of copperworks and investments aimed directly at air protection (e.g., up-to-date dust extraction technologies) enabled substantial reduction in the emission of heavy metals to the environment.

Constant monitoring of agricultural and food products contamination with heavy metals in the areas surrounding copperworks worldwide is of key significance in protecting human health and the ecology. Monitoring changes in the level of pollutants, due to investments in environmental protection is necessary for the proper evaluation and potential verification of industrial activities (Jakubowski, 2004; Jasiński, 2003; Rembiałkowska, Kacprzak, & Sokołowska, 2001; Żechałko-Czajkowska et al., 1997).

The study was aimed at assessing food products of plant origin originating from areas of two copperworks Głogów and Legnica, in terms of their contamination with arsenic, in view of a considerable improvement in environment conditions in those areas, resulting from recently reduced dust emissions.

2. Materials and methods

The studied foods were cereal grains (wheat, barley, triticale, rye), potatoes, vegetables (carrot, beetroots, cabbage, parsley root and leaves, tomatoes), and fruits (apples, pears). A total of 137 samples were examined that were collected between September and October 2005, both from crop fields or gardens, all in the full stage of maturity. The study was carried out on products originating from the protection zone of copperworks Legnica and from the area of copperworks Głogów (protection zone and areas outside the zone). Samples were collected by staff of the Chair of Human Nutrition in the presence of farm owners and copperworks representatives.

Samples of potatoes and root vegetables were precisely washed, dried, peeled and comminuted. Leaf vegetables, after removal of external or damaged leaves, were washed, dried and comminuted. Fruits were washed, dried and comminuted without peeling but after removal of cores with stones, since they are usually consumed in that form. Parts of comminuted field samples (500–800 g each) constituted an average laboratory sample, stored until analysed in the frozen state (−18 °C). Cereal grain, after removal of impurities, was ground and each ca. 500-g sample was stored at room temperature (Norma europejska, 2002; Norma polska, 2003).

Contents of arsenic were determined by atomic absorption spectrometry (AAS) using a Perkin–Elmer apparatus (Walthane, MA) with an MHS-10 unit for hydride generation (acetylene/argon), after previous "wet" mineralisation of the samples with nitric acid and hydrogen peroxide, according to Polish Standard PN-59/A-04010. The determination limit of arsenic was 0.00003 μg/ml. In order to verify the results obtained, apart from a calibration curve, use was also made of the standard addition technique. The average recovery of arsenic reached 97%. Results were analysed with Statistica 6.0 Software (StatSoft Inc., Tulsa, OK).

3. Results and discussion

The presence of chemical pollutants, including heavy metals, is one of the main criteria in food safety evaluation. Limiting contents of heavy metals in food products is essential, and usually regulations concerning that problem are, to a great extent, a compromise between realistic expectations and the possibilities of producing food with satisfactorily low levels of contaminants.

Permissible levels of food products contamination with heavy metals, valid in Poland for the last 30 years (Monitor Polski, 1993), have been changing, both in respect of the quantity and type of limited elements, as well as limits stipulated for individual metals. Before Poland's accession to the European Union, a regulation of the Minister of Health of 13th January 2003 (Dziennik Ustaw, 2001), on the maximum levels of contaminants in food products, limited permissible values for lead, cadmium, arsenic and mercury. After implementation of regulations of the European Union in Poland, arsenic levels are limited only in chosen foodstuffs, mainly seafood. For this reason, the results obtained in determinations of arsenic were referred to previously binding maximum permissible levels of that metal.

Table 1
Contents of arsenic in plant products from the area of copperworks Głogów in mg/kg of product and in % of permissible levels valid over the experimental period (Dziennik Ustaw, 2004; Dziennik Ustaw, 2005)

No.	Product	As content (mg/kg of product)			Adopted reference levels (mg/kg)	% of permissible level	
		x_{min}	x_{max}	$\overline{X} \pm SD$		$\overline{X}$	Range
1	Wheat ($n = 12$)	0.025	0.093	0.056 ± 0.021	0.2	28.0	12.3–46.6
2	Rye ($n = 3$)	0.074	0.195	0.115 ± 0.069	0.2	57.6	37.3–97.6
3	Triticale ($n = 5$)	0.032	0.078	0.050 ± 0.019	0.2	24.8	15.9–39.3
4	Barley ($n = 7$)	0.0072	0.111	0.047 ± 0.035	0.2	23.3	3.6–55.9
5	Potatoes ($n = 16$)	0.0008	0.058	0.021 ± 0.020	0.2	10.4	0.4–29.2
6	Carrot ($n = 13$)	0.0034	0.035	0.019 ± 0.010	0.2	9.7	1.7–17.6
7	Beetroot ($n = 11$)	0.0022	0.029	0.012 ± 0.009	0.2	6.2	1.1–14.7
8	Cabbage ($n = 8$)	0.0006	0.040	0.017 ± 0.015	0.2	8.6	0.3–19.8
9	Parsley root ($n = 11$)	0.0037	0.030	0.016 ± 0.009	0.2	7.9	1.9–15.2
10	Parsley leaves ($n = 12$)	0.0065	0.137	0.053 ± 0.038	0.2	26.5	3.2–68.4
11	Tomatoes ($n = 9$)	0.0003	0.027	0.005 ± 0.009	0.2	9.0	0.2–70.0
12	Apples ($n = 12$)	0.0023	0.034	0.014 ± 0.009	0.2	6.6	1.2–17.0
13	Pears ($n = 6$)	0.0175	0.034	0.020 ± 0.007	0.2	11.0	9.1–17.1

Table 2
Contents of arsenic in plant products from the area of copperworks Legnica in mg/kg of product and in % of permissible levels valid over the experimental period (Dziennik Ustaw, 2004; Dziennik Ustaw, 2005)

No.	Product	As content (mg/kg of product)			Adopted reference levels (mg/kg)	% of permissible level	
		x_{min}	x_{max}	$\overline{X} \pm SD$		$\overline{X}$	Range
1	Apples ($n = 6$)	0.0110	0.030	0.020 ± 0.007	0.2	10.0	5.5–15.3
2	Pears ($n = 6$)	0.0171	0.045	0.032 ± 0.1000	0.2	16.1	8.6–22.3

A total of 32 samples of cereal grains from 13 towns were collected for analyses. Arsenic content was determined in 16 samples of wheat grain, 7 samples of barley grain (including 2 samples of winter barley), in 5 samples of triticale grain, 3 sample of rye grain and in 1 sample of oat grain. Results obtained in this study for arsenic contents of plant products originating from the regions of copperworks Głogów and Legnica were presented in Tables 1 and 2, in the form of mean values and standard deviations, minimal and maximal values, median and in reference to standard values adopted according to the presented criteria. The mean content of arsenic in the cereal grains examined, except for rye, was low and accounted for ca. 25% of the stipulated permissible level. In rye grain the mean concentration of that element reached 57.5% of the value accepted as permissible. Contents of arsenic in the experimental samples of potatoes ranges from 0.0008 to 0.0583 mg/kg (mean: 0.0208 mg/kg). In 47% of the sample, its concentration fluctuated between 17% and 29% of the permissible level adopted in this study. The concentrations of arsenic in parsley roots ranged from 1.9% to 15% of the permissible level, with the mean content reaching 0.016 mg/kg. The content of arsenic in the examined samples of parsley leaves from the Głogowski region oscillated between 0.006 and 0.137 mg As/kg (mean: 0.0530 mg/kg). Arsenic contents in all samples of that product were below the maximum permissible level. Concentrations of that element ranged from 3.2% to 68% of the permissible values adopted in this study. Slightly higher contents of arsenic were observed by Grajeta (1987) in examining tomatoes and parsley leaves from industrialised areas. Considerably higher quantities of arsenic were reported by that author in vegetables originating from areas of a former mine and steelworks in Złoty Stok. Concentrations of arsenic in the analysed samples of carrot ranged from 0.0034 to 0.0351 mg/kg. Its content did not exceed 18% of the adopted permissible level. Similar results were obtained by Grajeta (1987), who examined carrot originating from industrialised areas (0.04–0.012 mg/kg). Substantially higher contents of arsenic were reported by that author in carrot from the areas of Złoty Stok and Błotnica (0.30 and 0.20 mg/kg, respectively). In most of the tomato samples, concentrations of arsenic did not exceed, 3% of the permissible levels adopted in the study. Also in the samples of apples and pears arsenic contents did not raise doubts and oscillated from a few to several per cents of the permissible level (mean: 0.014 mg/kg). The examined samples of vegetables and fruits were found to contain from 0.002 to 0.079 mg As/kg. In no samples analysed did the concentration of arsenic exceed the permissible level.

4. Summary

Contents of arsenic in the examined products originating from the area of copperworks Głogów and Legnica were low and in most of the samples were within a few to several per cents of the permissible level valid before 2004. Those values were adopted in the study as reference values, since currently permissible levels of those elements in food products are no longer stipulated.

Based on sparse, available literature data it may be concluded that the contamination level of the examined food products with heavy metals is lower or similar to contamination of those products in other non-industrialised regions of the country.

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References

Bieniek, K., & Sałacki, T. (1996). Stan środowiska województwa legnickiego. *Pediatria Polska, 4*(Suppl.), 61–66.

Concha, G., Vogler, G., Lezcano, D., Nermell, B., & Vahter, M. (1998). Exposure to inorganic arsenic metabolites during early human development. *Toxicological Sciences, 44*, 185–190.

Dziennik Ustaw (2001). nr 9, poz. 72. Rozporządzenie Ministra Zdrowia z dnia 27 grudnia 2000 roku w sprawie wykazu dopuszczalnych ilości substancji dodatkowych i innych substancji obcych dodawanych do środków spożywczych lub używek, a także zanieczyszczeń, które mogą znajdować się w środkach spożywczych lub używkach.

Dziennik Ustaw (2004). nr 120, poz. 1257. Rozporządzenie Ministra Zdrowia i Opieki Społecznej z dnia 30 kwietnia 2004 r. w sprawie maksymalnych poziomów zanieczyszczeń chemicznych i biologicznych, które mogą znajdować się w żywności, składnikach żywności, dozwolonych substancjach dodatkowych, substancjach pomagających w przetwarzaniu albo na powierzchni żywności.

Dziennik Ustaw (2005). nr 2, poz. 9. Rozporządzenie Ministra Zdrowia z dnia 22.12.2004 r. zmieniające rozporządzenie w sprawie maksymalnych poziomów zanieczyszczeń chemicznych i biologicznych, które mogą znajdować się w żywności, składnikach żywności, dozwolonych substancjach dodatkowych, substancjach pomagających w przetwarzaniu albo na powierzchni żywności.

Grajeta, H. (1987). Zawartość arsenu w warzywach pochodzących z okolic niektórych zakładów przemysłowych. *Roczniki PZH, 37*(4–5), 340–343.

Jakubowski, M. (2004). Monitoring biologiczny narażenia na czynniki chemiczne w środowisku pracy. *Instytut Medycyny Pracy*.

Jasiński, A. (2003). Efekty działań KGHM Miedź S.A. na rzecz ochrony powietrza w zagłębiu miedziowym. Materiały Konferencji Naukowej: Środowisko a zdrowie dzieci, Fundacja na Rzecz Dzieci Zagłębia Miedziowego, Legnica.

Monitor P. (1993). nr 22, poz. 233. Zarządzenie Ministra Zdrowia i Opieki Społecznej z dnia 31 marca 1993 roku w sprawie wykazu substancji dodatkowych dozwolonych i zanieczyszczeń technicznych w środkach spożywczych i używkach.

Norma europejska (2002). EN 13804:2002 Artykuły żywnościowe – Oznaczanie pierwiastków śladowych. Kryteria sprawności, zasady ogólne i przygotowanie próbek.

Norma polska (2003). PN – EN 13804:2003 Artykuły żywnościowe – Oznaczanie pierwiastków śladowych. Kryteria sprawności, zasady ogólne i przygotowanie próbek.

Piotrowski, J. (2006). *Podstawy Toksykologii*. Warszawa: WNT.

Rembiałkowska, E., Kacprzak, H., & Sokołowska, J. (2001). Jakość zdrowotna warzyw ekologicznych i konwencjonalnych z dawnego woj. kieleckiego. *Bromatologia i Chemia Toksykologiczna, 34*(1), 49–57.

Rocznik statystyczny GUS (2004). Warszawa.

Tong, S., Von Schimding, E. Y., & Prapamontol, T. (2000). Environmental lead exposure: A public health problem of global dimensions. *Bulletin of the WHO, 78*(9), 1068–1077.

Tsuji, J. S., Benson, R., Schoof, R. A., & Hook, G. C. (2004). Health effect levels for risk assessment of childhood exposure to arsenic. *Regulatory Toxicology and Pharmacology, 39*, 99–110.

Żechałko-Czajkowska A., Orzeł D., Styczyńska M., Figurska-Ciura D., Bronkowska M. (1997). Ocena zanieczyszczenia metalami ciężkimi produktów żywnościowych z rejonu oddziaływania Huty Miedzi "Głogów" w latach 1995–97. Sprawozdanie z wykonania badań. Akademia Rolnicza, Wrocław.