Research Article

Monika Sujka, Urszula Pankiewicz*, Radosław Kowalski, Artur Mazurek, Katarzyna Ślepecka, Magorzata Góral

Determination of the content of Pb, Cd, Cu, Zn in dairy products from various regions of Poland

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Abstract: The toxicity of heavy metals and their capacity for accumulation in the human organism make it necessary to conduct monitoring of their concentration in food. The objective of the study was to determine the content of lead, cadmium, copper and zinc in milk and dairy products from various regions of Poland: the Lublin Region, Podlasie, Podkarpacie, and Silesia. The study showed the presence of the analysed heavy metals in most of the products. The content of lead was related to the level of industrialisation of a region. Higher levels of Pb were found in products from Silesia than in those from the other regions. The study revealed the presence of cadmium in 50% of the samples. Its content varied in range from 0.0067 to 0.0058 mg/kg. The levels of Cu and Zn concentration in the analysed products were within broad ranges, from 0.0015 to 4.94 mg/kg and from 0.01 to 56.44 mg/kg, respectively. In the case of all analysed elements an increase in their concentration was noted in cheese spreads and cottage cheeses. No relationship was found between the content of heavy metals in the analysed products, and the region of their origin.

Keywords: heavy metals; dairy foods; ICP- MS.

1 Introduction

Heavy metals are among the most dangerous contaminants in the environment, though many of them, under suitable conditions, play the role of bioelements necessary for

correct functioning of the human body, e.g. zinc, iron, copper and selenium [1].

So far, no biological role has been demonstrated that could be played by mercury, cadmium, arsenic and lead, and they are considered to be substances totally alien to the human organism and harmful, even at very low concentrations. Common traits of mercury, lead and cadmium include ease of absorption from atmospheric air and from the alimentary tract, ease of penetration through the placenta, through the blood-brain biological barrier (Hg, Pb), ability to form complexes with macromolecules, and causing damage to the structure of the nucleic acids chains (Cd, Hg) [2, 3].

Toxic elements, e.g. cadmium, are absorbed with food and drinking water. Therefore, they can undergo bioaccumulation in products of animal origin and inclusion in the human food chain [3]. Long-term exposure of the human organism to even small doses of heavy metals, resulting from constant presence in a contaminated environment, may be the cause of subclinical changes, often irreversible, revealing themselves after many years, e.g. leukaemia. Milk and its products, e.g. cheeses, kefir, butter etc., as basic sources of animal protein, most vitamins and minerals, and common elements of human diet, are at the same time the main source of heavy metals and should be subjected to permanent control of the concentration of those metals [4]. Monitoring studies on products of animal origin (milk, eggs) indicate a considerable variation in the concentration of Cd, Hg, Pb and other heavy metals, from trace levels to amounts exceeding the maximum allowable concentrations many times [5]. In Poland, as in the whole European Union, limits have been laid down for the level of those metals in food products, and limitations on their emission have been imposed [6-8]. The content of those metals in milk and its products differs significantly in regions with industrial contamination and areas ecologically clean, therefore they are considered as indicators of contamination of the environment and food. Their concentration in food products varies in relation to:

***Corresponding author: Urszula Pankiewicz**, Department of Analysis and Evaluation of Food Quality, University of Life Sciences in Lublin, Lublin, Poland, E-mail: monika.sujka@up.lublin.pl

Monika Sujka, Radosław Kowalski, Artur Mazurek, Katarzyna Ślepecka, Magorzata Góral, Department of Analysis and Evaluation of Food Quality, University of Life Sciences in Lublin, Lublin, Poland

the content of a given element in soil, fodder, water and air, the level of bioavailability, and also the phenomenon of inter-elemental interactions [9, 10].

Heavy metals, even though they occur in small amounts, are a serious threat to the human organism, causing e.g. anaemia, neurological changes, dementia, psychic disturbances, inhibition of enzyme activity, disturbances in the absorption of iron, osteoporosis, damage to the kidneys, muscular atrophy, as well as cancers of the mouth, lungs, genital glands [11-14].

Milk is the basic raw material for the production of many food products and is the fundamental element in infant and child feeding, and therefore should have suitable quality and its content of heavy metals should be monitored as a matter of priority.

The objective of the study was to determine the content of lead, zinc, cadmium and copper in milk and dairy products from various regions of Poland (the Lublin Region, Silesia, Podlasie and Podkarpacie).

2 Materials and methods

2.1 Materials

Products for analyses were purchased in supermarkets. The choice of dairy companies whose products were analysed depended on the varied level of industrialisation of the particular regions of the country, and thus on various levels of environmental contamination. The Lublin Region (LA and LB) and Podlasie (P) are examples of regions with lower levels of industrialisation, Podkarpacie (PK) is a region with a medium level of industrialisation, while Upper Silesia (SA and SB) was chosen as a representative of the most industrialised regions of Poland. The letters A and B denote two different producers, while the numbers 1-5 are the number of products from a given assortment. After purchasing, the products were kept in their original packing at a temperature of -18°C, and subjected to analyses before the expiry of the “use by” date.

To determine the effect of raw material concentration and various production processes on the content of lead, cadmium, copper and zinc, 40 products from all assortment groups of a given producer (milk, butter milk, kefir, yoghurt, cream, cheese spread, cottage cheese) were analysed.

2.2 Measurement of water content

Water content of lyophilisates and products was determined with the use of a moisture analyser (Radwag WPS50SW) after drying samples at 100°C. Analysis was carried out in triplicate.

2.3 Lyophilisation

Samples of dairy products were lyophilised in a Labconco freeze dryer (Model 64132, Kansas City, MO, USA). Obtained lyophilisates were stored in an exicator and used for further analyses.

2.4 Determination of lead, cadmium, copper and zinc concentration

The samples obtained were ground using an analytical mill and an analytical balance was used to weigh samples of ca. 0.5 g, with an accuracy of 0.0001 g. The weighed portions were transferred to teflon tubes and flooded with 10 cm³ HNO₃ (Suprapur-Merck). After closing, the tubes were placed in the rotor of a mineraliser. Mineralisation was conducted in a microwave oven, CEM Mars Xpress, at a temperature of 210 degrees Centigrade and a pressure of approximately 7 atmospheres. The obtained clear mineralisates were transferred quantitatively to measurement flasks with volume of 50 cm³ and diluted with demineralised water (conductivity 0.055 µS/cm) up to the mark. The obtained solutions were analysed by means of a mass spectrometer with coupled plasma induction (ICP Mass Spectrometer Varian MS-820). The gas used for plasma generation was argon, from the company Messer, with a purity of 99.999%. In the analysis no reaction chamber (CRI) was used. The following settings of the apparatus were applied:

- Plasma Flow – 16 dm³/min.,
- Nebuliser Flow – 0.98 dm³/min.,
- RF Power – 1.38 kW,
- Sampling Depth – 6.5 mm.

The following isotopes of the analysed elements were used: ⁶⁵Cu, ⁶⁶Zn, ¹¹⁴Cd, ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb.

The determination was made with the method of standard curve. For the analysis, Ultra Scientific standards were used, with a purity of 99.999%. The results were expressed in mg/kg of fresh matter. During the analysis the analytical quality was controlled by means of

Table 1: Validation parameters applied during analysis.

Element	LOD [mg/kg]	LOQ [mg/kg]	Precision [%]	Recovery [%]	Uncertainty [%]
Cd	0.004	0.007	2.42	99	6
Pb	0.005	0.01	6.07	99	12
Cu	0.027	0.055	2.47	96	10
Zn	0.049	0.098	3.09	100	14

Table 2: Content of lead, cadmium, copper and zinc [mg/kg product] in milk from various regions of Poland.

	Pb	Cd	Cu	Zn
LA	0.012±0.004 ^{a*}	0.0000±0.0000 ^a	0.360±0.110 ^a	4.83±1.43 ^a
LB	0.013±0.003 ^a	0.0001±0.0000 ^a	0.310±0.081 ^a	2.58±0.66 ^a
SA	0.234±0.079 ^b	0.0000±0.0000 ^a	1.033±0.350 ^b	15.84±3.74 ^b
PTWI ¹ (µg/kg body mass)	25	7	3.5	7

* Means in the column denoted by a different letter are significantly different ($p < 0.05$).

¹Provisional tolerable weekly intake (recommended by the JECFA [16])

Table 3: Content of lead, cadmium, copper and zinc [mg/kg product] in kefir from various regions of Poland.

	Pb	Cd	Cu	Zn
LA	0.156±0.022 ^a	0.0000±0.0000 ^a	1.250±0.220 ^a	15.68±1.59 ^a
LB	0.010±0.002 ^b	0.0005±0.0001 ^b	0.194±0.050 ^b	2.79±0.56 ^b
SB	0.004±0.000 ^b	0.0007±0.0002 ^b	0.126±0.030 ^b	1.92±0.38 ^b
P	0.097±0.002 ^c	0.0000±0.0000 ^a	0.920±0.180 ^a	9.05±0.12 ^c
PK	0.006±0.001 ^b	0.0004±0.0001 ^b	0.087±0.020 ^b	1.69±0.32 ^b
PTWI ¹ (µg/kg body mass)	25	7	3.5	7

* Means in the column denoted by a different letter are significantly different ($p < 0.05$).

¹Provisional tolerable weekly intake (recommended by the JECFA [16])

measurement of a blind sample, a double sample, and the certified reference material “NIST-1577c Bovine Liver”.

2.5 Statistical analysis

The data were analysed using one-way analysis of variance (ANOVA) to examine the statistical significance of differences in the mean concentration of heavy metals determined in milk and its product samples. The probability level of $P = 0.05$ was considered statistically significant.

Ethical approval: The conducted research is not related to either human or animal use.

3 Results

The conducted analyses revealed the presence of the analysed heavy metals in most of the dairy products. Content of lead in milk from various regions amounted to a maximum of 0.013 mg/kg (Table 2). In dairy products of the type of kefir, yoghurt, buttermilk and cream, the content of lead varied in the range from 0.0039 mg/kg in yoghurt from Silesia (Table 5) to 0.156 mg/kg in kefir from the Lublin Region (Table 3). An elevated content of that element was noted in cream from Silesia – 0.143 mg/kg (Table 6). In cheese spreads the concentration of lead varied from 0.015 mg/kg in the product from the Lublin Region to 0.34 mg/kg in the product from Silesia. The highest accumulation of lead was found in cottage cheeses

Table 4: Content of lead, cadmium, copper and zinc [mg/kg product] in butter milk from various regions of Poland.

	Pb	Cd	Cu	Zn
SA	0.039±0.008 ^a	0.0021±0.0004 ^a	1.720±0.260 ^a	8.51±0.71 ^a
LB	0.005±0.001 ^b	0.0004±0.0001 ^b	0.188±0.030 ^b	2.18±0.16 ^b
PTWI ¹ (µg/kg body mass)	25	7	3.5	7

* Means in the column denoted by a different letter are significantly different ($p < 0.05$).

¹Provisional tolerable weekly intake (recommended by the JECFA [16])

Table 5: Content of lead, cadmium, copper and zinc [mg/kg product] in yoghurt from various regions of Poland.

	Pb	Cd	Cu	Zn
LA1	0.099±0.020 ^a	0.0000±0.0000 ^a	0.850±0.170 ^a	8.81±0.62 ^a
LA2	0.078±0.020 ^a	0.0000±0.0000 ^a	0.690±0.130 ^a	8.43±0.51 ^a
LB1	0.069±0.010 ^a	0.0000±0.0000 ^a	0.930±0.150 ^a	9.32±0.74 ^a
LB2	0.004±0.001 ^b	0.0004±0.0001 ^b	0.099±0.020 ^b	0.01±0.00 ^b
SB1	0.015±0.002 ^{cd}	0.0067±0.0010 ^c	0.138±0.020 ^c	2.68±0.24 ^c
SB2	0.021±0.004 ^d	0.0011±0.0003 ^d	0.260±0.030 ^d	3.76±0.28 ^d
SB3	0.004±0.001 ^b	0.0004±0.0001 ^b	0.010±0.002 ^e	1.18±0.11 ^e
SB4	0.011±0.002 ^c	0.0029±0.0010 ^e	0.259±0.005 ^d	3.01±0.25 ^c
SB5	0.008±0.002 ^c	0.0009±0.0002 ^d	0.124±0.020 ^c	2.70±0.18 ^c
PTWI ¹ (µg/kg body mass)	25	7	3.5	7

* Means in the column denoted by a different letter are significantly different ($p < 0.05$).

¹Provisional tolerable weekly intake (recommended by the JECFA [16])

Table 6: Content of lead, cadmium, copper and zinc [mg/kg product] in cream from various regions of Poland.

	Pb	Cd	Cu	Zn
LA	0.036±0.007 ^a	0.0004±0.0001 ^a	1.140±0.120 ^a	5.36±0.43 ^a
LB	0.006±0.002 ^b	0.0009±0.0002 ^b	0.002±0.000 ^b	2.05±0.26 ^{bd}
SA	0.143±0.020 ^c	0.0026±0.0005 ^c	0.963±0.080 ^{ad}	5.42±0.48 ^a
SB	0.012±0.003 ^d	0.0001±0.0000 ^a	0.028±0.050 ^c	2.72±0.35 ^b
P	0.100±0.020 ^c	0.0000±0.0000 ^c	0.880±0.140 ^d	8.35±0.58 ^c
PK	0.009±0.002 ^d	0.0010±0.0003 ^b	0.021±0.005 ^c	1.98±0.23 ^d
PTWI ¹ (µg/kg body mass)	25	7	3.5	7

* Means in the column denoted by a different letter are significantly different ($p < 0.05$).

¹Provisional tolerable weekly intake (recommended by the JECFA [16])

- from 0.03 mg/kg in the product from Podkarpacie to 0.38 mg/kg in that from Silesia.

The study revealed the presence of cadmium in 50% of the samples of dairy products. The highest concentrations of that element, approximately 0.0067 mg/kg and 0.0058 mg/kg in each product, respectively, were noted in the

case of yoghurt (Table 5) and cheese spreads (Table 7) from Silesia, and cheese spread from the Lublin Region.

The content of copper in the dairy products varied within a broad range, from 0.0015 to 4.94 mg/kg. The highest concentration of that element was found in cheese spread from Silesia – 4.94 mg/kg (Table 7) and in cottage

Table 7: Content of lead, cadmium, copper and zinc [mg/kg product] in cheese spreads from various regions of Poland.

	Pb	Cd	Cu	Zn
LA	0.051±0.010 ^a	0.0058±0.0010 ^a	1.150±0.130 ^a	7.72±0.62 ^a
LB1	0.072±0.010 ^{af}	0.0000±0.0000 ^b	1.794±0.270 ^b	8.32±0.58 ^a
LB2	0.015±0.004 ^b	0.0016±0.0005 ^c	0.082±0.020 ^a	3.71±0.29 ^b
SA1	0.340±0.050 ^c	0.0000±0.0000 ^b	4.940±0.440 ^c	56.44±2.78 ^c
SA2	0.021±0.004 ^b	0.0000±0.0000 ^b	1.086±0.140 ^a	5.34±0.42 ^d
SA3	0.180±0.030 ^{dg}	0.0066±0.0010 ^a	1.530±0.190 ^b	11.2±0.67 ^e
SA4	0.210±0.040 ^{dg}	0.0022±0.0005 ^c	2.850±0.310 ^d	19.36±0.96 ^f
P1	0.120±0.020 ^{ef}	0.0000±0.0000 ^b	3.740±0.280 ^e	12.4±0.86 ^e
P2	0.092±0.020 ^f	0.0000±0.0000 ^b	1.080±0.180 ^a	9.69±0.58 ^g
P3	0.220±0.030 ^g	0.0000±0.0000 ^b	1.610±0.170 ^b	17.2±1.37 ^f
PK	0.028±0.005 ^b	0.0017±0.0005 ^c	0.530±0.050 ^f	5.16±0.31 ^d
PTWI ¹ (µg/kg body mass)	25	7	3.5	7

* Means in the column denoted by a different letter are significantly different ($p < 0.05$).

¹Provisional tolerable weekly intake (recommended by the JECFA [16])

Table 8: Content of lead, cadmium, copper and zinc [mg/kg product] in cottage cheese from various regions of Poland.

	Pb	Cd	Cu	Zn
LA	0.340±0.040 ^a	0.0000±0.0000 ^a	3.940±0.260 ^a	53.72±1.61 ^a
LB	0.039±0.007 ^b	0.0026±0.0010 ^b	1.308±0.240 ^b	11.21±0.67 ^b
SA	0.380±0.060 ^a	0.0000±0.0000 ^a	2.220±0.190 ^c	52.47±1.31 ^a
PK	0.030±0.005 ^b	0.0010±0.0003 ^b	0.406±0.050 ^d	5.39±0.43 ^c
PTWI ¹ (µg/kg body mass)	25	7	3.5	7

* Means in the column denoted by a different letter are significantly different ($p < 0.05$).

¹Provisional tolerable weekly intake (recommended by the JECFA [16])

cheese from the Lublin Region – 3.94 mg/kg (Table 8), while the lowest – in cream from the Lublin Region – 0.002 mg/kg (Table 6) and in yoghurt from Silesia – 0.01 mg/kg (Table 5).

The level of zinc concentration in the analysed products varied within a very broad range, from 0.01 mg/kg in yoghurt from the Lublin Region (Table 5) to 56.44 mg/kg in cheese spread from Silesia (Table 7). The lowest content of zinc was noted in cream (1.98 mg/kg) and kefir (1.69 mg/kg) from Podkarpacie (Table 3 and Table 6), and also in kefir from Silesia (1.92 mg/kg) (Table 3), the its highest content was noted in cottage cheese from the Lublin Region (54 mg/kg) and from Silesia (52 mg/kg) (Table 8). As in the case of lead, copper and cadmium, and also in the case of zinc, an increase of concentrations were observed in cheese spreads and cottage cheeses.

4 Discussion

Lead contaminating the environment can originate both from natural sources (e.g. volcanic eruptions) and from human activity (batteries, motor vehicle exhaust gases, fertilisers, pesticides, insecticides, lead-based paints, tobacco smoke, water pipelines). The most often indicated source of milk contamination with lead is residues of that element in animal fodder and in water, but also in materials used for packing [15]. WHO set the acceptable daily intake (ADI) of lead at the level of 0.428 mg, while the more often used index, provisional tolerable weekly intake (PTWI), currently amounts to 25 µg per 1 kg of body mass, both for adults and for children [16]. In accordance with the Regulation of the Commission (EC) No. 1881/2006 of 19th December, 2006 (with subsequent revisions) [8], setting

the highest allowable levels of certain contaminants in food products, the maximum allowable level of lead in milk is 0.02 mg/kg fresh matter [17]. The content of lead in consumable milk from the Lublin Region did not exceed that norm. The permissible level of lead was exceeded 10-fold in the milk from Silesia. Dobrzański et al. [10] demonstrated a statistically significantly higher content of lead in milk from an industrial area relative to an area considered to be free of industrial pollutants; the content of lead in milk from the area of Upper Silesia was 0.042 mg/kg, while in milk from an area considered to be clean (Lower Silesia) – 0.019 mg/kg. Also, Radzymińska et al. [18] reported the statistically significant difference in the concentrations of lead between dairy products originating from different regions of Poland (central, western and south eastern). Our study showed a correlation between the content of lead in dairy products and the level of industrialisation of a region. Average contamination of milk with lead in Poland in the years 1998-1999 was at the level of 0.005 mg/kg, and in 2000 it decreased to 0.004 mg/kg [19]. In studies by Szkoda et al. [20] and Górka et al. [21], lead concentration in cow's milk was determined to be at the level of 0.003 mg/kg. In other European countries the Pb content in milk (mg/kg) was as follows: Slovenia – 0.05 and Spain – 0.0018 [22], Austria – 0.0065 [23], Italy – 0.0013 [24] and Romania – from 0.052 to 0.617 mg/kg [25]. Mean lead content in milk from Turkey was 0.0335 mg/kg [26], from Iran – 0.0129 mg/kg [27], from Mexico – 0.03 mg/kg [28] and from Pakistan – from 0.001 to 1.428 mg/l [29]. The results of Pb content determination in yoghurt reported by Khan et al. [30] indicated that this product may contain a much higher concentration of this toxic element (4.21 - 24.50 ng/g) than milk (3.35 ng/g). The study by Kulek de Andrade et al. [31] also showed that the content of lead in yoghurt can depend on production process because samples of a drinkable yoghurt contained a higher amount of this element than a pasty one. The concentration of lead in curd and cheese reported by Castro-Gonzalez et al. [28] was comparable to or higher than in milk. The authors concluded that it was due to increasing the protein content (lead has an affinity for protein) and decreasing the moisture level during cheese production.

Milk and dairy products represent about 20% of food consumption in Europe, similarly to cereals and vegetables [32]. According to Chary et al. [33] food originated from plant, mostly plant roots, is the main source of lead in human diet. The studies show that this element appears also in the milk of lactating animals fed contaminated grass [33] and consequently goes on to the human diet.

Monitoring of the content of lead in food is extremely important due to its high toxicity. Accumulation of lead in the human organism leads to a disturbance in the activity of many enzymes and in the functions of structural proteins. The best documented is the effect of Pb^{2+} on the enzymes of the respiratory chain, glycolysis pathway and the synthesis of hem, the effect of which are disturbances in the metabolic transformations of cells, such as: regulation of energetic processes, synthesis of proteins and nucleic acids [34]. Lead is a mutagenic element and can cause cancer, disturbances of the haematopoietic system and the central nervous system, and in addition it has the ability of passing through the placenta [1].

Cadmium is an element that is totally useless for the human organism. Its toxic effect is related mainly with its occurrence in the form of free cadmium ions that bind with atoms of sulphur, hydrogen and oxygen, causing disturbances in various metabolic cycles. Cadmium disturbs the metabolism of proteins and the transformation of vitamin B1. In cases of chronic poisoning it affects the metabolism of calcium and phosphorus compounds, impairs correct mineralisation of bones, and thus increases their fragility. Cadmium is classified among elements with a carcinogenic effect, and its embryotoxic and teratogenic effects are also confirmed [35]. The main source of soil contamination with cadmium is industry, phosphorus fertilisers and wastes. In nature that metal does not occur in a free state, but it is present primarily in sulphide ores of zinc, copper or lead, and also in fossil fuels, e.g. coal. Their mining and processing liberates considerable amounts of cadmium to the atmosphere, hydrosphere and soil [36], from which that toxic metal migrates into food. The standards pertaining to food do not specify the maximum allowable content of cadmium in dairy products, however, the JCA (Joint Committee of Experts of FAO/WHO for Food Additives) determined the PTWI for that element at the level of 7 µg/kg of body mass [16]. Based on the results obtained it is not possible to confirm any correlation between cadmium content and the region of origin of the products. Pietrzak-Fiećko et al. [37], who studied cadmium content in milk from Podlasie and from the Province of Łódź, also did not find such a correlation. Górka et al. [21], Szkoda et al. [20] and Żmudzki et al. [38] demonstrated in their studies that cadmium content in milk amounted to 0.0039 mg/kg, <0.001mg/kg and 0.003 mg/kg, respectively. In milk from Bieszczady, cadmium was found at a concentration of 0.002 mg/l [39]. In cow's milk from the area of the Warmińsko-Mazurskie Province and from the area of the Beskid Średni Mountains cadmium content was assayed at the level of 0.003 mg/kg [39,40]. In milk from the

Lublin Region cadmium was found at the concentration of an average of 0.006 mg/kg [39], and in milk from the District of Siedlce – at the level of 0.00039 mg/kg [21]. Significantly higher contents of cadmium in dairy products from central Poland than from western and south-east regions of the country were reported by Radzymińska et al. [18]. Dobrzański et al. [10] report cadmium content in milk within the range from 0.0035 mg/kg to 0.0083 mg/kg. For comparison, cadmium content in milk from highly developed countries, such as Italy, Spain and Austria, was at the level of 0.00002 mg/kg, 0.00047 mg/kg and 0.0007 mg/kg, respectively. In turn, the average content of cadmium in milk from the territory of Iran was 0.002 mg/l [41], from Pakistan - it ranged from 0.001 to 0.053 mg/l [29], and in cow's milk from Saudi Arabia the level of 0.0047 mg Cd/kg was determined [42]. According to Kulek de Andrade [31] the content of Cd in yoghurts varies from 2.5 to 12.4 ng/g, depending on the yogurt kind. Khan et al [30] obtained Cd concentrations in the range from 1.36 to 2.22 ng/g and they were even lower than those determined for plain milk.

Contamination of the environment with copper is caused by its presence in industrial (electronic industry, mining industry, copper metallurgy) and municipal sewage, and also in dusts emitted by metallurgical plants [43]. Copper is a component of many enzymes which take part in metabolic pathways responsible for energy generation in the cell (cytochrome c oxidase), free radicals scavenging (superoxide dismutase), formation of collagen and elastin (lysyl oxidase), production of catecholamines (dopamine β -monooxygenase) or melanin (tyrosinase) [44]. Therefore, as opposed to cadmium and lead, it is an element essential for the correct functioning of the human organism. An excessive level of copper in the organism can, however, lead to serious disorders, e.g. allergies, hyperthyroidism, hepatic cirrhosis, and infections [45]. For copper, WHO established PTWI at the level of 3.5 mg/kg of body mass [46]. As zinc reduces copper assimilation in cows, its content in milk and in milk products is much lower than that of zinc [24]. The results obtained in our study are similar to those presented by other authors. Licata et al. [24] report that the content of copper in milk from Italy varied in the range from < 0.136 to 737.58 μ g/kg. Parween et al. [29] obtained the results of Cu determination in milk in the range of 0.001 to 0.098 mg/l. The results determined in milk and yogurts from South Korea ranged from 137.9 to 718.3 ng Cu/g [30], whereas yoghurts from Brazil contained from 34 to 61 ng Cu/g [31]. Cheese spreads and cottage cheeses contain significantly more copper compared to the remaining assortment, which is the result of raw material concentration in the production process.

A similar conclusion was formulated by Maas et al. [47]. On the basis of the results obtained it is not possible to determine any correlation between the content of copper in the analysed products and the regions of their origin.

The source of the environmental pollution with zinc is the combustion of fossil fuels (coal, petroleum oil and its products) as well as industrial and municipal sewage. Due to its easy solubility, zinc contained in mining and industrial waste can migrate to the ground waters. Certain preparations used for plant protection, as well as phosphorus fertilisers, are an additional source of contamination with that element [48]. Zinc, like copper, is a main structural element and regulates the activity of a number of enzymes, has antioxidant properties and plays a role in the maintenance of the redox equilibrium in the cell [49, 50]. Excessive levels of zinc are harmful, and may lead to e.g. asthenia, vomiting, anaemia, insomnia, or neurodegenerative diseases [50]. According to WHO, the value of the PTWI index for zinc is 7 mg/kg of body mass [46]. Values of zinc concentration in dairy products reported by other researchers are similar to those obtained in our study. Maas et al. [47] obtained for milk (France) the range of 20.62–30.96 μ g Zn/g DM, and for cheese – 33.66–63.41 μ g/g DM. In milk and dairy products from Egypt, zinc concentration was found to be in the range of 2.73–18.316 ppm [51]. The concentration of that element in milk from Italy fell within the range of 24.73–4961 μ g/kg [24], while milk and yoghurts from South Korea contained this element in concentrations from 3535.6 to 4754.3 ng/g [30].

5 Conclusions

The concentration of lead, cadmium, zinc and copper increases with the level of raw material concentration in the production process and attains the highest values in cheese spreads and cottage cheeses. No correlation was found between the content of cadmium, copper and zinc and the level of industrialisation of the region from which the products originates, as opposed to lead, the content of which is the highest in products from Silesia.

Conflict of interest: Authors declare no conflict of interest.

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