

OCCURRENCE OF SELECTED CHEMICAL ELEMENTS IN MILK AND DAIRY PRODUCTS FROM RETAIL CHAINS IN SLOVAKIA

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Abstract

This work provides new data on the levels of some essential elements and toxic elements, important for their nutritional and/or toxicological properties, in some Slovak dairy products to evaluate the contribution of this food group to the quality of the Slovak diet. The aim of this study was to determine the concentrations of essential elements (Ca, Mg, Na, K, Zn, Mo) and toxic elements (Al, Ag, Li, Sb, Sr, Ba) in milk and dairy products available on the markets of Slovakia from two producers. From the essential elements the highest concentrations were recorded for Ca and K in the category of cheeses and milk. Significantly high level of Na was found in the cheese category. Of the toxic elements, in the case of Al, the highest permissible limit set by Slovak legislation was found to be exceeded in almost all dairy products. Numerous correlations between concentrations of elements in milk and dairy products were observed.

Keywords: chemical elements, milk, dairy products, markets

1. INTRODUCTION

Milk and dairy products are important components of the human diet. Milk has been described as a complete food because it contains vital nutrients including proteins, essential fatty acids, lactose, vitamins, and minerals in balanced proportions. However, milk and dairy products can also contain chemical hazards and contaminants, which constitute a technological risk factor for dairy products, for the related commercial image and, above all, for the health of the consumer (Licata et al., 2004).

Milk and dairy products contain more than 20 microminerals and microelements, some of which are necessary (essential) and required in minimum quantities in the human diet, i.e. iron (Fe), zinc (Zn), copper (Cu), selenium (Se), while others are not required for human health, i.e., chromium (Cr) and nickel (González-Montaña et al., 2019). Milk also contains the toxic elements aluminum (Al), arsenic (As), cadmium (Cd), lead (Pb) and mercury (Hg); their toxic effects include a number of ailments such as kidney and liver failure, muscle atrophy, bone damage, osteoporosis, hormonal and gastrointestinal disorders, dementia, mental disorders, inhibition of enzyme activity, iron absorption disorders, disorder of the nervous, immune, reproductive, cardiovascular and development systems, metabolic disorders such as anemia, and many others (Ismail et al., 2019; Brocca and Salvatore, 2022).

The minimum consumption of milk and milk products per person given by World Health Organization (WHO) should be at least 220 kg per year. In the Slovak Republic this consumption is evaluated on the level of 160 kg/person/year (Petrířák et al., 2017). The industrial processing of milk has long tradition in Slovakia, however, for the last 17 years, the consumption of drinking milk decreases in average by 0.998 kg per person per year, excluding consumption of cheese, sour milk products and butter (Kubicová et al., 2014). The milk products are considered as the most important source of calcium in the diet, as well as more than 20 different minor and trace elements (Gonnelli et al., 2009; Kurajdová et al., 2015). Generally, dairy products are important source of minerals and proteins essential for development and growth and health in humans. Nevertheless, they can contain some contaminants as the results of increasing environmental pollution (Kazi et al., 2009; Capcarová et al., 2017). The presence of various trace elements in dairy products is an indicator of qualitative parameters of the food and can image both, utility and beneficially aspects (calcium, phosphorus, iron, sodium, and others), but also hazardous condition concerning expect for environmental pollution as well as sanitation, hygiene conditions, used tools, machines and packaging lines (Capcarová et al., 2017; Capcarová et al., 2019). Toxic elements

may be harmful at low concentrations when ingested the long time. On the other hand, the essential elements indispensable for human organism can cause toxic effects in higher doses received for long time (Ulozlu et al., 2009). At any rate, the determination in dairy products is very useful in the assessment of the quality of food (Khan et al., 2014).

Therefore, this study was conducted to quantify the concentrations of essential and toxic elements in milk and dairy products and to assess the suitability and safety of these products when including these products in the diet of children and consumers.

2. MATERIALS AND METHODS

2.1. Materials

The samples of commercially available milk and dairy products were purchased from different markets in Nitra city, Slovak Republic in 2020. All samples of milk and dairy products were from two different producers. Monitoring of the occurrence of chemical elements was carried out during a 6-month monitoring period in 2020, from January to June. A total of 96 samples of milk and dairy products were obtained: milks (n= 24), cheese (n= 24), other dairy products – butter, sour cream, whipped cream etc. (n= 48).

The samples were left in their original packages and transferred to the lab in an ice box. Subsequently, samples of milk and dairy products were stored in marked plastic laboratory tubes and stored in a freezer (-20 °C) until analysis.

2.2. Methods

The following 12 elements were analyzed in all milk samples and samples of dairy products: Ag, Al, Ba, Ca, K, Li, Mg, Mo, Na, Sb, Sr, Zn. The content of selected elements was determined in samples of milk and dairy products by inductively coupled plasma optical emission spectrometry (ICP-OES). As a first step, the pre-analytical procedure was made. All the chemicals used during the sample preparation were highly pure. Until the sample processing, they were stored in freezer at -20 °C. Weight of the experimental samples ranged from 0.5 to 2.0 g and was reflected in measurement. The samples were mineralized in the high-performance microwave digestion system Ethos UP (Milestone Srl, Sorisole, BG, Italy) in a solution of 5 mL HNO₃ ≥69.0% (TraceSELECT®, Honeywell Fluka, Morris Plains, USA), 1mL H₂O₂ ≥30%, for trace analysis (Sigma-Aldrich, Saint – Louis, Missouri, USA) and 2mL of ultrapure water (18.2 MΩ cm⁻¹; 25 °C, Synergy UV, Merck Millipore, France). Samples, including the blank sample, were digested according to method for animal tissue developed and recommended by manufacturer to achieve the most reliable results. The method consists of heating and cooling phases. During the heating stage the samples were warmed to 200 °C for 15 min and this temperature was maintained for another 15 min. Afterwards, during the cooling phase, the samples underwent the active cooling for 15 min to reach the temperature of 50 °C. The digests were filtered through the VWR Quantitative filter paper 454 (particle retention 12 – 15 μm) (VWR International, Leuven, France) into the volumetric flasks and filled up with ultrapure water to a volume of 50 mL. Analysis of the elements (Ag, Al, Ba, Ca, K, Li, Mg, Mo, Na, Sb, Sr, Zn) was carried out using inductively coupled plasma - optical emission spectrometer (ICP OES 720, Agilent Technologies Australia (M) Pty Ltd.) with axial plasma configuration and with auto-sampler SPS-3 (Agilent Technologies, Switzerland).

The limits of detection (LOD) and limits of quantification (LOQ) were evaluated for the validation of the analytical method (Table 1).

Table 1. LOD and LOQ values for analyzed elements in milk and dairy products (µg/kg)

	Ag	Al	Ba	Ca	K	Li	Mg	Mo	Na	Sb	Sr	Zn
LOQ	1.0	0.67	0.10	0.03	1.00	0.20	0.03	1.67	0.5	6.67	0.03	0.67
LOD	0.3	0.2	0.03	0.01	0.3	0.06	0.01	0.5	0.15	2.0	0.01	0.2

LOQ- limit quantification; LOD- limit detection

2.2.1. Statistical analysis

Statistical analysis of the data was performed using Statistica Cz version 10 (TIBCO Software, Inc., Palo Alto, CA, USA). Differences in concentrations of the analyzed chemical elements between group of producers were compared by the ANOVA and Student's t-test. All data were expressed as mean and standard deviation. The relationships between the levels of individual metals in samples of milk and dairy products were calculated using Pearson's correlation analysis. A probability level of $p < 0.05$ was considered statistically significant.

3. RESULTS

The chemical elements were expressed as the mean $\pm$ SD (standard deviation). Concentrations of 12 elements in milk and dairy products from retail markets are shown in Table 2 – Table 5. All 12 chemical elements were detected in almost all monitored products. The exception was molybdenum, which was below the LOD in some products, as shown in Tables 2-5.

3.1 Concentrations of essential elements

From 12 chemical elements, which were detected in this study, essential elements were: Ca, Mg, Na, K, Zn, Mo. In group of milks, there was no statistically significant difference in the concentrations of essential elements between the monitored producers (Table 2). The highest concentrations were detected in case of Ca and K in all types of monitored milks from both of producers.

In case of cheese group (Table 3) statistically significant difference between producers was detected in case of eidam cheese in concentration of K, in parenica cheese in concentration of Ca and Na and in case of melted cheese in concentration of Ca, K and Zn. All statistically significant differences in this group of cheese were evident at the level $P < 0.05$. In both of producers, the highest concentrations of Ca and Na were found in all types of cheese.

In group of liquid dairy products, the most significant differences ($P < 0.05$) of essential elements were found between producers in case of Zn concentration in creamy yogurt and in concentrations of Ca, K and Mg in sour cream. In all type of liquid dairy products of this study, the highest concentration of K was detected in both of producers (Table 4).

In category solid dairy products (Table 5) statistically significant differences ($P < 0.05$) between producers were found in concentrations Ca, K, Mg and Zn in case of "bryndza" cheese and in concentration of Mg in cream spread.

3.2 Concentration of toxic elements

From toxic elements, which were detected in milks and dairy products from retail market were Ag, Al, Li, Sb, Sr, Ba.

In group of milks was found statistically significant difference ($P < 0.05$) in concentration of Sr between producers in case of pasteurized milk with 3.5% fat (Table 2).

In cheese group, statistically significant difference between producers ($P < 0.05$) were recorded in eidam cheese in concentration of Li, in parenica cheese in concentration of Li and Sb and in melted cheese in concentration of Ba, Li and Sr (Table 3).

By analyzing concentrations of toxic element in liquid dairy products were found statistically significant differences ($P<0.05$) between producers in concentration of Li in creamy yogurt and sour cream (Table 4). In cases of others toxic elements in liquid dairy products, there was no statistically significant differences between producers.

From group of solid dairy products, statistically significant differences between producers were found in concentrations of Sb and Sr in “brynzda” cheese and in concentration of Ba in cream spread ($P<0.05$).

The highest concentrations of toxic elements in monitored milk and dairy products were detected in case of Al, Sr and in group of solid dairy products also in case of Sb.

Table 2. Mean concentrations (mg/kg) followed by standard deviation of chemical elements in the milks

	UHT (1.5 % fat)		UHT (3.5 % fat)		Pasteurized (1.5 % fat)		Pasteurized (3.5 % fat)	
	Producer 1	Producer 2	Producer 1	Producer 2	Producer 1	Producer 2	Producer 1	Producer 2
Ag	0.004±0.005	0.003±0.002	0.003±0.004	0.002±0.001	0.003±0.003	0.002±0.0005	0.004±0.003	0.002±0.001
Al	0.231±0.279	0.153±0.180	0.345±0.485	0.259±0.407	0.186±0.315	0.531±0.608	0.227±0.361	0.583±0.609
Ba	0.056±0.023	0.081±0.058	0.046±0.021	0.095±0.080	0.099±0.114	0.065±0.033	0.042±0.024	0.063±0.032
Ca	846.993±51.462	905.67±186.332	836.232±70.620	840.585±105.477	817.994±93.567	880.026±183.439	800.418±131.098	822.234±107.006
K	1119.603±65.999	1177.646±201.374	1074.469±115.797	985.410±221.989	1137.947±101.192	952.422±300.699	1043.864±154.247	1014.246±136.468
Li	0.006±0.007	0.006±0.007	0.002±0.002	0.002±0.002	0.002±0.001	0.002±0.001	0.001±0.001	0.002±0.002
Mg	78.819±4.893	85.194±13.438	77.418±6.787	76.106±11.849	79.098±7.171	76.378±7.582	74.744±10.325	76.475±8.190
Mo	0.034±0.084	ND	ND	0.009±0.023	ND	ND	ND	ND
Na	327.085±20.946	355.521±63.13.1	300.496±35.450	287.616±68.861	316.848±31.751	282.384±97.379	292.095±44.399	302.343±40.765
Sb	0.001±0.0003	0.053±0.127	0.001±0.0005	0.001±0.0005	0.001±0.0005	0.001±0.0005	0.001±0.0005	0.001±0.0005
Sr	0.2673±0.030	0.364±0.030	0.266±0.033	0.333±0.051	0.265±0.041	0.335±0.113	0.251±0.037 ^a	0.325±0.060 ^b
Zn	3.077±0.313	3.077±0.313	2.903±0.427	2.951±0.461	2.921±0.390	3.168±1.144	2.699±0.477	2.8524±0.402

^{a,b} Different letter in rows indicate statistically significant differences between producers

Table 3. Mean concentrations (mg/kg) followed by standard deviation of chemical elements in different types of cheese

	Eidam (45 % fat)		Polooštiepok ¹		Parenica ²		Melted cheese	
	Producer 1	Producer 2	Producer 1	Producer 2	Producer 1	Producer 2	Producer 1	Producer 2
Ag	0.003±0.004	0.0024±0.002	0.002±0.0001	0.004±0.006	0.004±0.002	0.004±0.001	0.003±0.003	0.002±0.0001
Al	1.422±1.560	1.901±1.986	2.537±2.713	1.896±2.586	1.896±2.586	1.439±1.579	5.689±4.000	2.337±2.028
Ba	0.489±0.121	0.509±0.087	0.358±0.166	0.329±0.167	0.454±0.084	0.479±0.053	0.239±0.060 ^a	0.334±0.078 ^b
Ca	6127.405±476.596	5949.832±846.893	4580.249±1853.546	3958.427±1509.502	5285.67±228.91 ^a	5961.726±211.58 ^b	2343.682±149.273 ^a	2900.823±306.846 ^b
K	878.693±77.046 ^a	729.769±88.732 ^b	845.139±359.074	994.2703±309.669	834.525±162.61	879.187±101.20	1917.197±45.456 ^a	1037.186±40.886 ^b
Li	0.017±0.005 ^a	0.032±0.007 ^b	0.016±0.007	0.0245±0.001	0.0225±0.001 ^a	0.015±0.011 ^b	0.011±0.006 ^a	0.039±0.007 ^b
Mg	242.259±14.818	227.842±30.225	169.566±41.350	165.399±34.581	188.481±146.73	216.008±6.30	135.425±4.032	126.758±10.766
Mo	ND	ND	ND	ND	ND	ND	ND	ND
Na	4569.917±915.332	4974.368±1113.445	4504.74±1339.360	4887.405±1509.069	5050.815±526.49 ^a	3818.227±624.85 ^b	5671.612±180.073	5514.567±235.177
Sb	0.001±0.005	0.032±0.077	0.167±0.408	0.169±0.208	0.167±0.412 ^a	0.169±0.326 ^b	0.167±0.408	0.167±0.408
Sr	2.442±0.198	2.664±0.308	1.808±0.734	1.764±0.729	2.007±0.113	2.438±0.102	1.121±0.034 ^a	1.636±0.067 ^b
Zn	26.453±2.544	26.923±3.842	22.073±9.307	18.402±7.694	26.416±1.812	27.726±1.365	9.039±0.728 ^a	13.837±1.214 ^b

^{a,b} Different letter in rows indicate statistically significant differences between producers

^{1,2} typical Slovak traditional cheese

Table 4. Mean concentrations (mg/kg) followed by standard deviation of chemical elements in different types of liquid dairy products

	Creamy yogurt		Whipped cream		Sour cream		Fermented milk	
	Producer 1	Producer 2	Producer 1	Producer 2	Producer 1	Producer 2	Producer 1	Producer 2
Ag	0.002±0.002	0.003±0.003	0.003±0.0001	0.002±0.0001	0.003±0.003	0.002±0.0001	0.002±0.0001	0.003±0.0004
Al	0.459±0.348	0.448±0.482	1.258±0.128	0.078±0.068	2.044±1.441	1.255±1.417	0.229±0.405	0.362±0.162
Ba	0.061±0.038	0.055±0.024	0.069±0.023	0.078±0.068	0.062±0.053	0.055±0.059	0.049±0.025	0.0612±0.038
Ca	649.449±100.474	715.674	540.809±71.396	543.101±53.160	631.522±63.986 ^a	603.392±91.461 ^b	782.891±89.086	982.186±362.955
K	830.447±171.369	928.8012±63.922	666.186±136.544	659.733±62.258	895.380±77.010 ^a	857.220±132.653 ^b	1025.8489±145.975	1245.911±512.551
Li	0.001±0.001 ^a	0.002±0.001 ^b	0.006±0.012	0.005±0.012	0.006±0.012 ^a	0.003±0.001 ^b	0.001±0.001	0.002±0.001
Mg	61.281±9.894	66.926±5.368	48.861±4.287	48.779±1.506	61.460±5.159 ^a	58.4732±9.960 ^b	74.263±9.905	92.065±35.548
Mo	ND	ND	0.010±0.024	0.012±0.029	ND	0.007±0.016	ND	ND
Na	222.520±50.697	261.799±18.716	175.336±40.327	172.418±18.034	244.926±28.110	233.754±41.497	289.795±47.976	371.269±152.605
Sb	0.001±0.0005	0.001±0.0005	0.167±0.408	0.187±0.205	0.167±0.408	0.167±0.408	0.001±0.0005	0.001±0.0005
Sr	0.2483±0.058	0.251±0.019	0.196±0.045	0.211±0.025	0.216±0.034 ^a	0.221±0.043 ^b	0.258±0.037	0.372±0.175
Zn	2.238±0.167 ^a	2.696±0.263 ^b	1.979±0.629	1.979±0.629	2.028±0.329 ^a	1.977±0.350 ^b	2.644±0.547	3.393±1.268

^{a,b} Different letter in rows indicate statistically significant differences between producers

Table 5. Mean concentrations (mg/kg) followed by standard deviation of chemical elements in different types of solid dairy products

	Butter		Sheep cheese "bryndza"		Cream spread		Curd	
	Producer 1	Producer 2	Producer 1	Producer 2	Producer 1	Producer 2	Producer 1	Producer 2
Ag	0.002±0.0005	0.002±0.0005	0.002±0.0005	0.002±0.0005	0.003±0.003	0.026±0.061	0.004±0.059	0.002±0.0001
Al	1.712±1.883	1.444±1.883	2.432±1.355	2.563±2.393	2.098±2.056	2.452±2.375	0.632±0.569	0.821±1.059
Ba	0.063±0.088	0.062±0.097	0.527±0.096	0.6230.217	0.092±0.052 ^a	0.232±0.123 ^b	0.050±0.041	0.082±0.029
Ca	136.256±49.624	183.621±66.054	3819.99±420.771 ^a	2816.192±256.277 ^b	666.057±70.319	2312.763±2044.259	775.406±43.818	815.412±89.043
K	164.703±9.974	181.097±8.873	770.581±27.395 ^a	1046.975±33.158 ^b	1303.158±181.667	1263.947±419.875	864.188±88.264	773.807±92.916
Li	0.005±0.012	0.014±0.024	0.032±0.010 ^a	0.047±0.006 ^b	0.002±0.002	0.007±0.005	0.002±0.002	0.003±0.002
Mg	12.971±1.460	14.2056±2.160	179.736±14.323 ^a	159.038±12.316 ^b	71.701±7.690 ^a	123.306±50.528 ^b	78.381±6.146	74.999±5.641
Mo	ND	0.023±0.037	ND	ND	0.018±0.044	ND	ND	0.018±0.043
Na	41.174±2.384	41.802±3.828	5559.462±252.256	5814.198±23.658	1566.495±197.115	2739.21±1630.235	249.713±31.216	239.772±35.283
Sb	0.167±0.408	0.167±0.408	0.167±0.108 ^a	0.189±0.101 ^b	0.167±0.408	0.167±0.408	0.167±0.008	0.214±0.401
Sr	0.036±0.018	0.055±0.031	2.218±0.237	2.039±0.458	0.242±0.032	0.892±0.872	0.303±0.028	0.341±0.026
Zn	1.486±1.041	0.456±0.285	15.193±1.864 ^a	9.801±1.333 ^b	2.02±0.384	9.959±8.009	5.411±0.164	6.5134±1.303

^{a,b} Different letter in rows indicate statistically significant differences between producers

3.3 Correlations between chemical elements in milk and dairy products

The correlation analysis showed some strong positive/negative and statistically significant correlations among the elements in each group of milks and dairy products.

In UHT milk (1.5% fat) were detected strong positive correlation ($P<0.01$) between Ba and Ca, K, Li, Mg, Na, Sr and Zn, strong positive between Ca and K, Li, Mg, Na, Sr, Zn ($P<0.01$), strong positive correlation between K and Li, Mg, Na, Sr, Zn ($P<0.01$), between Li and Mg, Na, Sr, Zn ($P<0.01$), between Mg and Na, Sr, Zn ($P<0.01$), between Na and Sr, Zn ($P<0.01$).

In UHT milk (3.5% fat) were detected strong positive correlations between Ca and Mg ($P<0.05$), between K and Mg, Na ($P<0.01$), between Mg and Na ($P<0.01$).

In pasteurized milk (1.5% fat) were found strong positive correlations between Al and Ca, Sr, Zn ($P<0.01$), between Ca and Al, Sr, Zn ($P<0.01$), between K and Mg, Na ($P<0.01$), between Mg and Na ($P<0.01$).

In pasteurized milk (3.5% fat) were found strong positive correlations between Ca and K, Mg, Na, Zn ($P<0.01$), between Ba and K ($P<0.05$), Sr ($P<0.01$), between K and Mg, Na, Zn ($P<0.01$), between Mg and K, Na, Sr, Zn ($P<0.01$), between Zn and Na ($P<0.01$).

Strong positive correlations in creamy yogurt were detected between Ca and K, Mg, Na ($P<0.01$) and Sr ($P<0.05$), between K and Ca, Mg, Na and Sr ($P<0.01$), between Mg and K, Na ($P<0.01$), between Na and Sr, Zn ($P<0.01$).

In fermented milk were found strong positive correlations between Al and Ba ($P<0.01$), Ba and Ca, K, Li, Mg, Na, Sr, Zn ($P<0.01$), between Ca and K, Mg, Na, Sr, Zn ($P<0.01$), between K and Li, Mg, Na, Sr, Zn ($P<0.01$), between Mg and Na, Sr, Zn ($P<0.01$), between Sr and Zn ($P<0.01$).

In eidam cheese were detected strong positive correlations between Al and Ba ($P<0.01$), Sr, Zn ($P<0.05$), Ba and Sr ($P<0.01$) and Zn ($P<0.05$), Ca and Mg, Zn ($P<0.01$), Sb ($P<0.05$), between K and Mg ($P<0.01$), between Mg and Zn ($P<0.01$), Mg and Sr ($P<0.05$), Sb and Sr ($P<0.01$), Sr and Zn ($P<0.01$).

In “parenica” cheese were found strong positive correlations between Ba and K ($P<0.01$), between Ca and Mg and Sr ($P<0.01$), strong negative correlation between Ca and Na ($P<0.01$), Ca and Zn ($P<0.05$), K and Mg and Li and Na ($P<0.05$), and between Mg and Sr ($P<0.01$).

In whipped cream were detected strong positive correlations between Al and Ba ($P<0.01$), between Ca and Sr ($P<0.01$), between K and Na ($P<0.01$), strong negative correlation between K and Sr ($P<0.01$), between Li and Sb ($P<0.01$), between Mg and Na ($P<0.05$) and strong negative correlation between Na and Sr ($P<0.01$).

In dairy product – curd was found strong positive correlations between Ca and Sb ($P<0.05$) and Zn ($P<0.01$), between K and Mg, Na ($P<0.01$), between Mg and Na ($P<0.01$), between Sb and Zn ($P<0.01$) and between Sr and Zn ($P<0.05$).

Strong positive correlations in cream spread were found between Ag and Sb ($P<0.05$), between Ba and Ca, Mg, Na, Sr, Zn ($P<0.01$), between Ca and Li, Mg, Na, Sr, and Zn ($P<0.01$) and strong negative correlation between Ca and K ($P<0.01$), strong negative correlations between K and Na, Sr, Zn ($P<0.01$), strong positive correlation between Li and Na, Sr, Zn ($P<0.01$), between Mg and Na, Sr, Zn ($P<0.01$), between Na and Sr, Zn ($P<0.01$).

In cheese “polooštiepok” strong positive correlation were detected between Ba and Ca, Li, Mg, Sr, Zn ($P<0.01$) and strong negative correlation between Ba and K ($P<0.01$), between Ca and Li, Mg, Sr and Zn ($P<0.01$) and strong negative correlation between Ca and K ($P<0.05$), strong negative correlations between K and Li, Mg, Sr, Zn ($P<0.01$), strong positive correlation between Li and Sr, Zn ($P<0.01$), between Mg and Sr, Zn ($P<0.01$).

In sour cream were found positive correlation between Ag and Li ($P<0.01$), between Ca and K, Mg, Na, Sr ($P<0.01$) and Zn ($P<0.05$), between K and Mg, Li, Na, Sr ($P<0.01$), between Mg and Na, Sr, ($P<0.01$), between Na and Sr ($P<0.01$), between Sb and Zn ($P<0.05$).

In melted cheese were detected positive correlation between Ca and Sr, Zn ($P<0.01$) and strong negative correlation between Ca and K ($P<0.01$), strong negative correlation between K and Li, Sr, Zn ($P<0.01$), strong positive correlation between Li and Sr, Zn ($P<0.01$), Sr and Zn ($P<0.01$).

In typical slovak dairy product “bryndza” were found strong positive correlation between Ag and Al ($P<0.01$), between Ca and Mg, Zn ($P<0.01$) and strong negative correlation between Ca and K ($P<0.01$), strong negative correlation between K and Zn ($P<0.01$) and strong positive correlation between Mg and Sr ($P<0.05$). In butter strong positive correlations were detected between Al and Ba ($P<0.01$) and Li ($P<0.05$), between Ca and Sr ($P<0.01$), between Li and Sr ($P<0.01$).

4. DISCUSSION

Detection, determination, and comparison of heavy metals in milk and dairy products to determine their safety have been a source of interest worldwide (Razei et al., 2014). The number of metals in uncontaminated milk and dairy products are admittedly minute, but the manufacturing and packaging processes may significantly alter their contents. Thus, heavy metals such as Al, Cd, Ni, Hg, Sb and Sr may contaminate different cattle or sheep feed and the environment. In this sense, the excretion into milk and following into dairy products at various levels is very likely (Ribeiro Sant'Ana et al., 2021).

Milk and dairy products are good sources of minerals. The consumption of dairy products is important in the preventing osteoporosis, proper development of bones and dental health (Weaver, 2014). This study showed that milk and dairy products from Slovak markets are rich in the content of element such as Ca, Mg and K. Calcium concentrations varied in milk from 800.418 to 905.48 mg/kg, Mg concentrations from 74.744 to 85.194 mg/kg and K concentrations from 952.422 to 1177.646 mg/kg. In group of cheese varied concentrations Ca from 2343.682 to 6127.405 mg/kg, concentrations of Mg from 126.758 to 242.259 mg/kg and concentrations of K from 729.769 to 1917.197 mg/kg. In group of liquid dairy products concentration of Ca varied from 540.809 to 982.186 mg/kg, Mg concentrations from 48.779 to 92.065 mg/kg and K concentrations from 659.733 to 1245.911 mg/kg. In the last group of solid dairy products, concentrations of Ca varied from 136.256 to 3819.99 mg/kg, concentrations of Mg from 12.971 to 179.736 and concentrations of K from 164.703 to 1303.158 mg/kg.

This study showed, that of all monitored products from the Slovak markets from 2 different producers, it was found that the highest Ca concentrations were detected in group of cheeses. This fact is mainly influenced by biochemical processes during cheese production. The loss of water content at various stages of production of hard cheese is one of the reasons of expected the enrichment in trace elements in comparison with fresh cheese or the others dairy products (Elbarbary and Hamouda, 2013; Barone et al., 2018). On the other hand, the highest Na concentrations were also found in the cheese group compared to the other milk or dairy products. However, these concentrations are greatly influenced by the technological processing of cheese, as these cheeses are usually stored in salt solutions during production. Despite the fact, that cheeses are an excellent source of Ca, from a health point of view it is important to include cheeses with a lower sodium content in the diet, especially for children.

From the point of view of the occurrence of toxic elements that were monitored in this work, were recorded very low concentrations in almost all milks and dairy products. Increased concentrations of Al can be considered as risk concentrations in category cheeses where the concentration of Al varied from 1.422 to 5.689 mg/kg at both producers and the same in the category solid dairy products, where the Al concentrations varied from 1.444 to 2.563 mg/kg. In category liquid dairy products Al concentrations was increased in case of sour cream (2.044 and 1.225 mg/kg). All these concentrations were higher compared to the highest permissible limit for milk and milk products according to Decree no. 2/1994 Coll. Decree of the Ministry of Health of the Slovak Republic, which establishing hygienic requirements for foreign substances in foodstuffs. The penetration of this element into these products was probably caused by storage containers during the processing of milk and dairy products, or by the packaging materials in which the products are packed. Compared to other toxic elements in this study, were noted increased values of Sr in category of cheeses and solid dairy products (1.121-2.664 mg/kg in both of producers). Toxic elements are elements that are not necessary for the organism and have an adverse effect on it even in low concentrations. The main source of exposure to these elements is diet (Waseem et al., 2014). Long-term consumption of foods containing toxic elements can cause their constant accumulation in the body and thus disruption of biochemical processes in various organs of the body (Mahmood and Malik, 2014; López-Alonso et al., 2017).

A benefit of presented study is correlations analysis of interaction between selected elements in milk and dairy products. As reported authors Rodríguez Rodríguez (1999), analyzes of correlation relationships between elements in milk and dairy products are described very rarely in the literature. Interaction between liver, kidney and muscle elements are more frequently described in the available literature compared to the milk (Blanco-Penedo et al., 2006; Issac et al., 2012). According to Alonso et al. (2004) it is caused by the fact, that these organs play the main role in trace element metabolism. In this study was found several strong negative/or positive correlation interactions between selected

elements in all milks or dairy products. The most common correlations were found between Ca, Mg, K, Na and Zn. Similar correlation relations, especially between Ca and Mg or Zn in milk were also described in the studies of authors Tomza-Marciniak et al., 2011; Pilarczyk et al., 2013 and Antunović et al., 2016.

5. CONCLUSIONS

The present study confirmed that milk and dairy products from Slovak markets are very rich in the content of essential elements. The consumption of these types of milk and dairy products from producers in this study may contribute to the daily dietary intake of important essential elements. On the other hand, however, the study revealed increased concentrations of aluminum in dairy products that exceeded the highest permissible limit according to the current Slovak legislation, which may ultimately have an impact on the accumulation of this element in the body of consumers. Because milk and dairy products are among the basic foods consumed by the most vulnerable groups of people, namely children and the elderly, it is essential to monitor presence of toxic elements in milk and dairy products.

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