THE CONTENT OF MACRO AND TRACE ELEMENTS IN CURD AND TRADITIONAL WHITE BRINED CHEESE

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Abstract. The content of macro and trace elements in curd samples and white brined cheese produced from raw ewes' milk using a traditional technology in different regions in Macedonia is the subject of this study. The cheese is manufactured in households located in regions exposed to different levels of anthropogenic pressure. The content of 19 elements (Ag, Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Sr, and Zn) is analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) after performed microwave digestion. The highest values of Ca, Mg, K and P are observed in curd samples collected from a household near the city of Skopje with concentration of 2139-3343 mg/kg, 103-196 mg/kg, 313-545 mg/kg and 942-1499 mg/kg, respectively. The cheese samples contain 732-4549 mg/kg (Ca), 35.8-176 mg/kg (Mg), 63-344 mg/kg (K), 496-2138 mg/kg (P) and 3231-12828 mg/kg (Na). The non-standardized procedures for cheese production and the low quality equipment for cheese production has affected the content of macro and trace elements in the end product. The content of Ag, As, Cd, Co, Ni and Pb in all of the analyzed samples was below the detection limit although some households are exposed to environmental contamination with heavy metals (Cd, Pb and Zn). In cheese, the content of Cu (2.49 to 8.08 mg/kg) shows higher content in all collected samples. The content of Fe is in the range of 3.81-12.09 mg/kg, Mn 0.12-0.70 mg/kg, Zn 4.21-18.33 mg/kg and Cr 0.04-0.14 mg/kg. The results of this study show that the traditional white brined cheese is safe for consumption.

Key words: Mineral elements, trace elements, curd samples, traditional cheese.

Introduction. Cheese and dairy products are an important part of the human diet and are considered healthy because of their nutritional values. The quality of the cheese was evaluated not only by its chemical and microbiological characteristics, but also by its content of minerals (Kirdar et al., 2013b). The concentration of minerals in cheese is variable and is affected not only by the milk composition, but also by the cheese making procedures and ripening conditions (Macedo & Malcata, 1997). The content of the mineral components like Ca, K, P, Mg in the milk is important because it has influence on the technological properties of the milk during the cheese making process as they participate in the coagulation, way drainage and curd samples texture (Lucey & Fox, 1993; González-Martín et al., 2011).

The content of trace elements and heavy metals in cheese can be increased as a result of their higher concentration in the environment, the processing equipment, reagents and accidental contamination during storage (Caggiano et al., 2005; Elbarbary & Hamouda, 2013). The negative impact of heavy metals on the human health as a result of increasing industrialization and environmental pollution has raised the interest in metal contamination of foodstuffs (Perween, 2015). Recently, many studies regarding mineral and heavy metal content in milk and cheese (Dobrzański et al., 2005; Anastasio et al. 2006; Vural et al., 2007; Aly et al., 2010; Kodrik et al., 2011; Lukáčová et al., 2012) and their variation during ripening and seasonal changes (Cichoscki et al., 2002; González-Martín et al., 2009, Kirdar et al., 2013a) have been conducted, due to this problem.

The production of white brined cheese in traditional manner is still present in Macedonia and the same is an economical and important trait of the rural districts. It is produced in small farms and households from raw ewe's milk without addition of starters, using traditional procedures and tools. However, there are few studies regarding the content of mineral elements and heavy metals, especially in cheese. The study of Ivanova et al. (2011) of the mineral content in milk from different dairy sheep breeds rose in agro ecological regions in Bulgaria and Macedonia showed a slight variation in the content of Ca and P while the content of trace elements was lower than the highest permissible levels for raw sheep milk.

The aim of this study is to assess the concentration of macro and trace elements in curd samples and white brined cheese since it is produced in a traditional way, using traditional tools and techniques. It was also important to assess whether the trace elements in the collected samples were in admissible amounts as the households from where the samples were collected were located in areas exposed to different levels of anthropogenic pressure.

Materials and methods

Sampling sites

The study was conducted in the course of May 2014 and the samples were collected from 12 households located in different regions in Macedonia exposed to different anthropogenic pressure. Three households (in the eastern region) are located near the lead and zinc mine "Sasa", two households (in the central region) are located near the abandoned lead and zinc smelter in Veles and one household (near Skopje) is located near the oil refinery. The households from Sveti Nikole (eastern region), Bistra Mountain (western region) and Mariovo (south-western region) are located in areas without any intensive sources of pollution.

The sheep flocks included mainly Merinolandschaft crossbreeds. During the whole year the flocks were fed on pastures with exception of the winter periods when the flocks were fed with grazing and hand feeding (with hay and barley or concentrates).

Sample collection

Total of 23 samples were collected. 11 samples from curd after milk curdling performed with commercial rennet and 12 samples from white brined cheese after 40 days of ripening. The cheese ripens in approximately 20% brine made of water and coarse salt. The exact quantity of the salt added in the brine was not measured. The samples of curd and cheese were collected in plastic containers and brought to the laboratory in refrigerated condition. Until the analyses were performed, the samples were kept frozen (-18 ºC).

Sample analyses

The curd samples and cheese samples were analyzed for content of macro elements (Ca, Mg, K, Na and P) and trace elements (Ag, Al, Ba, Cu, Fe, Mn, Sr, Zn, Ni As, Cr, Pb, Cd and Co). For all the samples a microwave digestion system ($Mars_x$, CEM) was used. The curd and cheese samples were first dried at 108 ºC and then were grated. A dried sample (0.5 g) was added with 7 ml HNO_3 (trace pure) and 2 ml H_2O_2. Then they were left overnight to react and burn the organic material. The vessels with the material were then put in a microwave digestion system for total digestion (15 min at 180 ºC). After the digestion, the samples were filtered and transferred in 25 ml flasks. After digestion all the samples were analyzed. The content of macro and trace elements was expressed as mg/kg wet weight.

The content of elements in samples was determined using inductively coupled plasma - atomic emission spectrometry ICP-AES, (715-ES Varian, USA) applying ultrasonic nebulizer CETAC (ICP/U-5000AT$^+$) for better sensitivity.

Statistical analyses

Statistical analyses were conducted using F-test and Pearson coefficient of correlation between the results obtained from curd samples and cheese samples. The analyses were performed using the software package Statgraph 3.0 (Statistical Graphics, Warrenton, Virginia, USA)

Results

The content of the macro elements in curd samples are presented in Table 1.

Table 1. **Content of macro elements in curd samples (mg/kg wet weight)**

Region	Household	Ca	Mg	K	Na	P
Sv. Nikole	1	2449	132	382	164	1064
	2	2198	126	313	171	942
	3	2593	146	360	152	1094
Av±Sd		2413±200b	135±10b	352±35b	162±10	1033±80b
Sasa	4	2228	126	327	135	955
	5	2474	160	488	183	1191
	6	2492	153	377	194	1087
Av±Sd		2398±148b	146±18b	397±82b	171±31	1077±118b
Veles	7	2738	152	467	732	1206
	8	2368	143	366	156	1048
Av±Sd		2553±262b	148±6ab	416±71ab	444±407	1127±112b
Mariovo	9	2139	103	400	157	992
	10	2517	173	409	256	1227
Av±Sd		2328±267b	138±50b	405±6b	206±70	1110±166b
Skopje	11	3343a	196a	545a	267	1499a
Av±Sd - Average±standard deviation, a,b - values in the same column with no common letters differ significantly (p<0.05)						

The content of Ca and P in curd samples from the Skopje region is significantly higher ($p < 0.05$) compared to the other analyzed regions, while the content of Mg and K in the curd samples from the Skopje region is significantly higher ($p < 0.05$) compared to the curd samples from the regions of Sv. Nikole, Sasa and Mariovo. With regard to the concentration of Na, the statistical analysis shows no significant differences between the regions.

The content of trace elements in curd samples collected from different households is shown on Table 2. The variation in their content between the samples is statistically significant ($p < 0.05$) only for the Al, Ba, Cu, Fe, Sr and Zn.

Table 2. **Content of trace elements in curd (mg/kg wet weight)**

Region	House hold	Al	Ba	Cr	Cu	Fe	Mn	Sr	Zn
Sv. Nikole	1	2.28	0.362	0.07	1.02	2.86	0.12	1.74	7.15
	2	3.68	0.437	0.06	0.84	4.26	0.09	1.31	5.80
	3	1.29	0.350	0.07	0.89	2.67	0.08	1.72	6.20
Av±Sd		2.42±1.20a	0.38±0.05ac	0.07±0.01	0.92±0.09b	3.26±0.87ab	0.09±0.02	1.59±0.25a	6.38±0.70b
Sasa	4	1.22	0.754	0.03	0.56	2.19	0.09	0.91	7.13
	5	2.15	2.164	0.03	1.13	4.26	0.17	1.17	9.23
	6	1.55	1.650	0.06	0.80	2.82	0.13	1.52	7.18
Av±Sd		1.64±0.47ab	1.52±0.71b	0.04±0.02	0.83±0.29b	3.09±1.06a	0.13±0.04	1.20±0.31ab	7.85±1.20b
Veles	7	2.94	0.326	0.07	0.88	4.61	0.15	0.99	8.19
	8	1.93	0.329	0.04	0.90	3.33	0.08	0.74	7.03
Av±Sd		2.43±0.71ab	0.33±0.002c	0.06±0.02	0.89±0.02b	3.97±0.91ab	0.12±0.05	0.86±0.18b	7.60±0.82b
Mariovo	9	2.30	1.005	0.03	0.82	3.34	0.08	1.18	8.21
	10	2.63	0.850	<0.01	0.82	3.55	0.12	1.35	7.23
Av±Sd		2.46±0.23ab	0.93±0.11abc	nd	0.82±0.001b	3.45±0.15ab	0.09±0.02	1.26±0.13ab	7.72±0.69b
Skopje	11	3.28b	0.496c	0.06	1.32a	4.96b	0.12	1.10b	11.62a

Av±Sd - average±standard deviation, nd - not detected, a, b, c - values in the same column with no common letters differ significantly (p<0.05)

As for the Co (<0.1 mg/kg) and the toxic elements such as Ag (<0.1 mg/kg), Cd (<0.02 mg/kg), Ni (<0.1 mg/kg) and Pb (<0.4 mg/kg) it can be noticed that in all tested samples the level of the elements is below the limit of detection, except in the sample collected from a farm in the region of Veles. The presence of As with concentration of 1.82 mg/kg in the curd samples is probably a result of additional contamination, since no arsenic was detected in the cheese sample collected from the same household. As for the concentration of Cr (Table 2) in the curd samples, it ranges within the limits <0.01-0.07 mg/kg which is similar to the results of Borys et al. (2006).

The content of the tested macro elements in the cheese samples collected from different regions presented in Table 3 show no statistically significant differences (p>0.05), except for potassium

Table 3. **Content of macro elements in cheese (mg/kg wet weight)**

Region	Household	Ca	Mg	K	Na	P
Sv. Nikole	1	1149	60.0	78.0	8913	660
	2	1260	50.7	85.9	9263	808
	3	4549	176	99.8	11826	2138
Av±Sd		2319±1932	96±70	88±11b	10001±1590	1202±814
Sasa	4	1321	62.6	104	12828	846
	5	834	50.7	142	7206	717
	6	732	35.8	63	7553	496
Av±Sd		962±315	49.7±13	103.1±40b	9195.6±3151	686.3±177
Veles	7	1576	115	344	12427	893
	8	1525	113	312	3231	890
Av±Sd		1550±36	114±1.0	328±23a	7829±6503	892±2.0
Mariovo	9	1085	53.2	92.2	7141	637
	10	1857	119	149	11608	909
Av±Sd		1471±546	86±46	121±40bc	9374±3158	773±193
Skopje	11	1493	72.6	116b	9347	876
Bistra	12	1252	120	181bc	4999	640

Av±Sd - average±standard deviation, a, b, c - values in the same column with no common letters differ significantly (p<0.05)

As for the content of trace elements (Table 4) there are differences between collected cheese samples but statistical significance (p<0.05) is present only for the content of Cu and Zn.

The toxic elements can originate from different sources such as industrial and municipal waste, vehicle emission and mining activities and can be widely dispersed in the environment. Analyses of As (<0.1 mg/kg), Ag (<0.1 mg/kg), Cd (<0.02 mg/kg), Co (<0.1 mg/kg), Ni (<0.1 mg/kg) and Pb (<0.4 mg/kg) in all collected samples were below the limit of detection.

Discussion

Changes in the content of macro elements in curd samples after milk curdling are expected (Table 1). The increased content of Ca, P and Mg in curd samples is a result of their ability to remain in insoluble or colloidal phase of milk (70-80% of Ca and P and 50% of Mg) (De La Fuente et al.,1997; Borys et al., 2006; Yabrir et al., 2014). The higher content of macro elements in the curd samples may also be a result of the traditional methods for production which implies that there are differences in the amount of added rennet, the time of curdling and the manner of curd samples processing.

Table 4. **Content of trace elements in cheese (mg/kg wet weight)**

Region	House hold	Al	Ba	Cr	Cu	Fe	Mn	Sr	Zn
Sv. Nikole	1	11.59	0.269	0.04	6.21	6.93	0.15	1.59	10.83
	2	3.87	0.157	0.06	5.89	8.67	0.25	0.68	8.90
	3	5.97	0.769	0.07	8.08	6.68	0.43	4.26	18.33
Av±Sd		7.14±3.99a	0.40±0.33	0.06±0.01	6.73±1.18a	7.43±1.08	0.28±0.14	2.18±1.86	12.69±4.98a
Sasa	4	3.15	0.363	0.05	6.51	12.09	0.26	1.46	10.65
	5	2.36	0.588	0.06	4.42	4.26	0.13	0.60	4.79
	6	1.44	0.616	0.04	2.80	3.91	0.15	0.78	5.71
Av±Sd		2.32±0.86b	0.52±0.14	0.05±0.01	4.58±1.86ab	6.75±4.63	0.18±0.07	0.95±0.45	7.05±3.15ab
Veles	7	3.11	0.229	0.04	3.34	5.37	0.34	1.11	7.72
	8	6.08	0.240	0.14	2.66	7.76	0.12	0.81	4.90
Av±Sd		4.60±2.10ab	0.23±0.01	0.09±0.07	3.00±0.48b	6.57±1.69	0.23±0.16	0.96±0.21	6.31±2.00ab
Mariovo	9	2.00	0.419	0.05	2.49	3.81	0.23	1.02	6.88
	10	3.27	0.672	<0.01	3.48	6.42	0.70	2.96	8.30
Av±Sd		2.64±0.89ab	0.55±0.18	nd	2.98±0.70b	5.12±1.84	0.47±0.33	1.99±1.37	7.59±1.00ab
Skopje	11	2.77ab	0.211	0.07	3.27b	4.47	0.31	1.55	6.56ab
Bistra	12	3.20ab	0.391	<0.01	2.50b	5.02	0.30	0.93	4.21b

Av±Sd - average±standard deviation, nd - not detected, a, b - values in the same column with no common letters differ significantly ($p<0.05$)

The variations in the content of trace elements in the curd samples collected from different regions (Table 2) are due to the ability of the elements to bind casein and stay in a higher percentage in the curd samples i.e. in the cheese. The highest value of Al (3.28 mg/kg) was observed in the curd samples collected from the farm in the vicinity of Skopje. Compared with the curd samples collected from the other examined regions a significant difference ($p <0.05$) was observed only in relation to the curd samples collected from the farms near Sasa. Elbarbary & Hamouda (2013) emphasized that the containers of low quality used in the production of cheese can contribute to the increase of the Al content. As for the highest content of Ba (Table 2), it was measured in the curd samples collected from the vicinity of Sasa, which is statistically significant at the level of $p <0.05$ compared with the curd samples collected from the regions of Sveti Nikole, Veles and Skopje. The available literature does not present data relative to the content of Ba in curd samples therefore it is not possible to make comparisons.

The content of copper in curd samples, shown in Table 2, is significantly higher ($p<0.05$) in the sample collected from the region of Skopje compared to the samples collected from other analyzed regions. The highest concentration of iron (4.96 mg/kg), measured in curd samples collected from the region of Skopje, shows a significant difference only in relation to the region of Sasa. The variations in the content of Cu and Fe in the curd samples are a result of partial distribution of these elements between the soluble and insoluble milk phase. Copper and iron are present in the insoluble phase of milk with 57% and 65% respectively (Yabrir et al., 2014). Some of these elements have the affinity to bind to molecules of low molecular weight such as citrate while the other part binds to the β-casein or the α_s casein (De La Fuente et al., 1997).

The trace elements like Zn and Mn remain in highest percentage (80-90%) in the colloidal phase tied to the casein micelles (De La Fuente et al., 1997; Borys et al., 2006; Yabrir et al., 2014) which results in more increased concentrations in the curd samples compared to the other elements. The variations in Mn concentration between regions have no statistical significance, while the highest concentration of Zn (11.62 mg/kg), measured in the curd samples collected from the region of Skopje, is significant when compared to the other analyzed regions. The variation in the content of trace elements is influenced by the method of cheese production but also by the additional input of elements from the utensils used during manufacturing (Güller, 2007; Elbarbary & Hamouda, 2013). When compared to the studies of Özlü et al. (2012), the concentrations of Fe and Cu in the curd samples of this study are higher, while the values of Zn and Mn are similar or lower.

Table 3 shows the values for the content of macro elements in the cheese. It can be noticed that the cheese from household 3 in the region of Sveti Nikole contains more Ca, Mg and P due to the cheese production technology. Additional warming of the curd samples is carried out during the production of this cheese, resulting in higher deposition of casein and secretion of whey in quantity higher than that of the other tested samples of cheese. Ca, Mg and P are elements that remain tied to the casein micelles in higher percentage, therefore their concentrations in the sample are higher. The statistical analysis shows significant difference ($p<0.05$) of K content between the samples from Sveti Nikole and Veles, Sveti Nikole and Bistra; Sasa and Veles; and Sasa-Bistra, Veles-Mariovo,Veles-Skopje, Veles-Bistra and Skopje-Bistra.

The decrease of the concentration of calcium, magnesium and phosphorus in relation to the curd samples which is related to the decrease of the pH value of the cheese during ripening is remarkable. In the curd samples, the pH-value of the samples was in the range of 6.45-6.80 while in the cheese that value was decreased to a level of 4.75-5.89. The decrease of the pH value causes migration of these elements from the colloidal into a soluble fraction and their excretion with the whey (Macedo & Malcata, 1997), which is also reflected by the correlation coefficient (for Ca $r = 0.540$, for P $r = 0.473$). Compared with the results of Macedo & Malcata (1997) and Borys et al. (2006), the cheese tested in this study contains lower content of Ca, Mg and P. The obtained results also shows resemblance or higher values compared to the study of Kirdar et al. (2013a, 2013b).

The cheese salting (brining), gives rise to the Na content in the cheese. Unlike sodium, there is no additional source of potassium during ripening and therefore its concentration is drastically decreased. Higher content of Na in the tested white brined cheese were found in relation to the results of Cichoscki et al. (2002); González-Martín et al. (2011) but the same were lower compared to the Macedo & Malcata (1997); Merdivan et al. (2004); Kirdar et al. (2013b).

The content of Al in cheese (Table 4) compared with the curd samples increases, and significant differences among the tested samples of cheese were observed only between the regions Sveti Nikole and Sasa. The cheese samples collected from household 1 of the region of Sveti Nikole contains the highest content of Al (11.59 mg/kg) compared with all of the tested samples. According to its characteristics aluminum binds more to the low-molecular compounds from the whey and together they are extracted from the cheese, but on the other hand the traditional method of production implies the use of low-quality containers for handling and ripening, and the low pH-value and cheese acidity can cause migration of Al from the vessels and cause additional contamination of the cheese (Elbarbary & Hamouda, 2013). In contrast to aluminum, the concentration of Ba in the cheese samples is decreased in relation to the curd samples, probably due to the distribution of Ba in higher proportion in the whey than in the casein. The highest content of Ba (0.769 mg/kg) was observed in the cheese produced in the third household in Sveti Nikole, which in turn is characterized with a different working technology. Also the content of Ba in the soil in this region is higher compared with the other locations (Stafilov et al., 2014) and through the animal feed the same can reach the milk and cheese. The variations of the Ba concentration between the cheeses produced in different regions are not statistically significant and are probably due to the traditional methods of production.

The highest content of Cu and Fe was observed in the cheese samples collected from the regions of Sveti Nikole and Sasa. The comparison of Cu values shows statistically significant variations ($p<0.05$) between the cheese samples collected from the region of Sveti Nikole and the samples collected from the regions of Veles, Mariovo, Skopje and Bistra. On the other hand, the statistical analysis of Fe values variation didn't show significant difference between the analyzed cheese samples. The content of Cu and Fe in the soil from the regions from where the cheese samples were collected shows high values especially in the regions of Sveti Nikole, Sasa and Veles as a result of the Pb-Zn mining and smelter activity (Stafilov et al., 2010, 2014) and the same can affect the animals' metabolism, their mineral status and prevalence in milk (Kodrik et al., 2011). Similar and lower content of Cu and Fe in cheese samples were obtained by Macedo & Malcata (1997), Aly et al. (2010), Cichoscki et al. (2002), Borys et al. (2006) and Özlü et al. (2012).

Zn and Mn are mostly associated with the casein fraction (Cichoscki et al., 2002) and that is why their content in the analyzed cheese samples were increased. Maximum content is observed in the cheese sample collected from the region of Sveti Nikole. The distinctions of Zn content between cheeses from different regions was significant only between the samples collected from Sveti Nikole and the Bistra region. This is expected since the region of Bistra is considered an area with a low anthropogenic impact while the region of Sveti Nikole is characterized with high mineral content in the soils.

The content of manganese varies in the range of 0.12-0.70 mg/kg with the maximum determinate value in the cheese from the Mariovo region. The coefficient of correlation ($r=0.662$ for Zn and $r= 0.488$ for Mn) shows that the variation of acidity and pH value during cheese ripening has probably influenced the content variation of these two elements (Cichoscki et al., 2002), as well as the distinctions during cheese production. The obtained content of Zn and Mn in this study is similar with the results of Borys et al. (2006), Aly et al. (2010), Özlü et al. (2012) and Kirdar et al. (2013a).

The increase of lead in cheese can be a result of the environmental contamination but also it can be influenced by using fodder for animal nutrition that is grown near highways, by using lead pipes and lead-lined containers for water supply (Elbarbary & Hamouda, 2013). As a possible source of cheese contamination, Moreno-Rojas et al. (2010) pointed out the salt used for cheese salting during production or ripening. The analyses of the salt used for brine preparation where the examined cheese was ripened and kept showed that the concentration of Pb was also under the limit of detection. The content of Cd in analyzed cheese samples (<0.02 mg/kg) is similar to the results of Borys et al. (2006) and Kodrik et al. (2011). Anastasio et al. (2006), Vural et al. (2007) and Tarakçi et al. (2010) found that the level of Cd in mature cheese was in the range of 0.06-0.15 µg/g dry weight, 0.1-0.6 µg/g and 0.03-0.26 µg/g dry weight. According to Orak et al. (2005) the concentration of Cd in white cheese was 0.127 µg/g. The differences in the geographical area, the characteristics of the equipment and the production practices didn't influence the content of Ni in analyzed cheese samples (<0.1mg/kg). Vural et al. (2007); Özlü et al. (2012) found that the content of Ni in Kashar and Herby cheese were 0.30 mg/kg and 0.8-4.8 µg/g, respectively. In Trappista cheese, made from cow milk, the concentration of Ni was in the range of 902.7-929.5 µg/kg and in white cheese from Turkey the same was 1.057 µg/g (Vural et al., 2007; Kodrik et al., 2011). The content of Cr in cheese samples didn't increase significantly compared to the curd samples. The values of Cr in cheese samples varied in the range of <0.01-0.14 mg/kg (Table 4). The increased levels of Cr are probably the result of its affinity to bind with the casein, and during curdling it is mainly moved to the cheese (Anastasio et al., 2006). However, statistical analyzes didn't show any significant differences in its concentration between the regions. The obtained results are in concordance with the results of Orak et al.(2005) and Borys et al. (2006). The Italian cheeses contain Cr with concentration of 0.47 µg/g dry weight (Caggiano et al., 2005; Anastasio et al., 2006). In the ewe's cheese from the Banat region the Cr concentration was higher and it varied in the range of 0.214-0.225 mg/kg, and in Herby cheese the same was in the range of 1.9-8.7 µg/g (Gogoasă et al. 2006; Vural et al., 2007). Kes cheese contained Cr in concentrations of 2.31-7.25 µg/g dry weight (Tarakçi et al., 2010).

Although some of the cheese samples were collected from the households exposed to higher anthropogenic pressure (Sasa Mine, Veles Smelter, Skopje Refinery), the results of the toxic elements analysis didn't show differences regarding the cheese samples collected from the regions with low anthropogenic influence (Sveti Nikole, Mariovo, Bistra).

Conclusions

The geographic regions characterized with specific compositions of the soil and pasture vegetation have influence on the mineral content of cheese, especially on trace elements. The non-standardized (traditional) procedures during cheese production, the production equipment of inferior quality have influence on the content of macro and trace elements in the end product. Samples collected from regions exposed to higher levels of pollution indicate that the content of toxic elements is below the limit of detection. Therefore, the traditional white brined cheese is safe for consumption. This study also suggests that more detailed analyses are necessary since there is small amount of published data in the Republic of Macedonia regarding this issue of research.

References

1. Aly M. M., Al-Seeni M. N., Qusti S. Y. and El-Sawi N. M. Mineral content and microbiological examination of some white cheesein Jeddah, Saudi Arabia during summer 2008. Food and Chemical Toxicology, 2010. 48. P. 3031-3034.

2. Anastasio A., Caggiano R., Macchiato M., Paolo C., Ragosta M., Paino S., Cortesi M. L. Heavy Metal Concentrations in Dairy Products from Sheep Milk Collected in Two Regions of Southern Italy. Acta Veterinaria Scandinavica 2006. 47. P. 69-74.

3. Borys M., Pakulski T., Borys R., Pakulska E. and Węgrzyn E.. The content and retention of some major and trace minerals in sheep's milk and cheese. Archiv fur Tierzucht, Dummerstorf 2006. 49. P. 263-267

4. Caggiano R., Sabia S., D'Emilio M., Macchiato M., Anastasio A., Ragostad M., and Paino S. Metal levels in fodder, milk, dairy products, and tissues sampled in ovine farms of Southern Italy. Environmental Research 2005. 99. P. 48–57.

5. Cichoscki J. A., Valduga E., Valduga A.T., Tornadijo M. E. and Fresno M.J. Characterization of Prato cheese, a Brazilian semi-hard cow variety: evolution of physico-chemical parameters and mineral composition during ripening. Food Control. 2002. 13. P. 329-336.

6. De La Fuente M. A., Olano A. and Juarez M. Distribution of calcium, magnesium, phosphorus, zinc, manganese, copper and iron between the soluble and colloidal phases of ewe's and goat's milk. Le Lait, 1997. 77. P. 515-520.

7. Dobrzański Z., Kołacz R., Górecka H., Chojnacka K. and Bartkowiak A. The content of microelements and trace elements in raw milk from cows in the Silesian region. Polish Journal of Environmental Studies 2005. 14. P. 685-689.

8. Elbarbary H. A. and Hamouda A. F. Variations in some heavy metals' level during processing of soft cheese. Food Measure. 2013. 7. P. 194-198.

9. Gogoasă I., Gergen I., Rada M., Pârvu1 D., Ciobanu C., Bordean D., Măruţoiu C.and Moigrădean D.. AAS detection of heavy metal in sheep cheese (the Banat area, Romania). Buletinul USAMV-CN 62. 2006. P. 240-245

10. González-Martín I., Hernández-Hierro J. M., Revilla I., Vivar-Quintana A., Lobos-Ortega I. and González-Pérez C. Changes in the mineral content in cheeses of different compositions during 6 months of ripening. Czech Journal of Food Sciencies 2009. 27. P. 114-118

11. González-Martín I., Hernández-Hierro J. M., Revilla I., Vivar-Quintana A. and Lobos-Ortega I. The mineral composition (Ca, P, Mg, K, Na) in cheese (cow's, ewe's and goat's) with different ripening times using near infrared spectroscopy with fibre-optic probe. Food Chemistry 2011. 127. P 147-152.

12. Güler Z. Levels of 24 minerals in local goat milk, its strained yoghurt and salted yoghurt (Tuzlu yoğurt). Small Ruminant Research 2007. 71. P. 130-137.

13. Ivanova T., Pacinovski N., Raicheva E., Abadjieva D. Mineral content of milk from dairy sheep breeds. Macedonian Journal of Animal Science 2011. 1. P. 67–71.

14. Kirdar S. S., Ocak E., Köse S. and Özer E. Seasonal changes in mineral and trace elements of Çanak cheese. Asian Journal of Chemistry 2013a. 25. P. 6177-6180.

15. Kirdar S.S., Ocak E., Köse S. Mineral and trace metal levels of Akçakatik cheese collected from Mediterranean Region-Turkey. Asian Journal of Chemistry 2013b. 25. P. 1643-1646.

16. Kodrik L., Wagner L., Imre K., Polyak K. F., Besenyei F. and Husveth F. The effect of highway traffic on heavy metal content of cow milk and cheese. Hungarian Journal of Industry and Chemistry 2011. 39. P. 15-19.

17. Lucey A.J., and Fox P.F. Importance of calcium and phosphate in cheese manufacturing: a review. Journal of Dairy Science 1993. 76. P. 1714-1724.

18. Lukáčová A., Massányi P., Agnieszka G. and Jozef G.. Concentration of selected elements in raw and ultra heat treated cow milk. Journal of Microbiology, Biotechnology and Food Science. 2012. 2. P. 795-802.

19. Macedo, A. C. and Malcata F. X. Changes of mineral concentrations in Serra cheese during ripening and throughout the cheese making season. The Journal of the Science of Food and Agriculture. 1997. 74. P. 409–415.

20. Merdivan M., Yilmaz E., Hamamci C. and Aygun R. S. Basic nutrients and element contents of white cheese of diyarbakır in turkey. Food Chemistry. 2004. 87. P. 163-171.

21. Moreno-Rojas R., Sánchez-Segarra P. J., Cámara-Martos F. and Amaro-López M. A. Heavy metal levels in Spanish cheese: influence of manufacturing condition. Food Additives and Contaminants 2010. 3. P. 90-100.

22. Orak H., Altun M. and Ercag E. Survey of heavy metals in Turkish white cheese. Italian Journal of Food Science 2005. 17. P. 95-100.

23. Özlü H., Aydemir Atasever M., Urçar S., Atasever M.. Mineral contents and heavy metal contamination in Kashar cheeses consumed in Erzurum province, Turkey. Journal of the Faculty of Veterinary Medicine, Kafkas University 2012. 18. P. 205-208

24. Perween R. Factors involving in fluctuation of trace metals concentrations in bovine milk. Pakistan Journal of Pharmaceutical Science 2015. 28. P. 1033-1038.

25. Stafilov T., Šajn R., Pančevski Z., Boev B., Frontasyeva M. V. and Strelkova L. P. Heavy metal contamination of surface soils around a lead and zinc smel¬ter in the Republic of Macedonia. Journal of Hazardous Materials. 2010. 175. P. 896-914.

26. Stafilov T., Balabanova B., Šajn R. Geochemical atlas of Bregalnica River Basin. Faculty of Natural Sciences and Mathematics, Ss Cyril and Methodius University, Skopje. 2014.

27. Tarakçi Z., Dervişoğlu M., Temiz H., Aydemir O. and Yazici F. Review on Kes cheese. Academic Food Journal 2010. 35. P. 283-288.

28. Vural A., Narin I., Erkan M. E. and Soylak M. Trace metal levels and some chemical parameters in herby cheese collected from south eastern Anatolia-Turkey. Environmental Monitoring and Assessment 2007. 139. P. 27-33.

29. Yabrir B., Hakem A., Mostefaoui A., Titouche Y., Bouzidi A. and Mati A. Nutritional value of Algerian breed ewe’s milk related to its mineral content. Pakistan Journal of Nutrition 2014. 13.P. 176-180.

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