

Fatty acid profiles and mineral content of Serbian traditional white brined cheeses

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Abstract

This study deals with fatty acid profiles and mineral contents of traditional Serbian white cheeses in brine. Study covered four Serbian traditional white brined cheeses: Zlatar cheese, Sjenica cheese, Svrљig cheese and Homolje cheese prepared from raw cow and ovine milk. Fatty acid profiles of traditional cheeses were qualitatively and quantitatively different. The content of saturated fatty acids was in the range of 65.97 %-76.61 % (cow cheeses) and 69.68 %-74.52 % (ovine cheeses). Unsaturated fatty acids range of cow and ovine cheeses was 23.39 %-34.03 % and 25.48 %-30.08 %, respectively. Depending on the type of cheese, the ratio of polyunsaturated fatty acids was 1.66 %-11.03 %. The lowest content of saturated fatty acids was observed in Sjenica cow cheeses. Thus, this type of traditional cheeses had the most favorable health indices including atherogenicity index (1.89), thrombogenicity index (1.37) and desirable fatty acid ratio (46.34 %). Mineral content of traditional cheeses was also different. The ratio Ca:P was in the range of 0.70-1.33. The highest level of Ca, P, K, Mg, Zn, Cu and Cr was detected in Sjenica cheeses prepared from cow milk. The absence of Cd was observed in all cheeses.

Key words: white cheese, fatty acid profile, mineral content

Introduction

Cheese is a significant source of fat in the human diet and contains a high variety of fatty acids. From a nutritional point of view, different cheese varieties contain a highly digestible fat. Its digestibility is in the range of 88-94 % (Renner, 1987). However, cheese is often presented by an adverse nutritional image due to the association between saturated fatty acids (SFAs), which are the major fatty acids of cheese, and cholesterol with cardiovascular diseases had. Although many researchers have considered SFAs as one of the contributory factors in heart disease, so far there has been no real study to demonstrate conclusively a direct link between cardiovascular disease and milk fat or to implicate dairy products in heart disease (Kanekanian, 2014). Moreover, cheese is a

rich source of a short chain fatty acids and certain trans-fatty acids that can be considered as part of a healthy diet (Lock et al., 2014).

Cheese fat contains saturated (SFA), mono-unsaturated (MUFA) and polyunsaturated fatty acids (PUFA). In general, milk fat contains approximately 66 % saturated (SFA) (57.4 % palmitic, 21.6 % myristic, and 17.6 % stearic), 30 % monounsaturated (MUFA), and 4 % polyunsaturated fatty acids (PUFA) (López-Expósito et al., 2012). Their ratio and composition in cheeses vary considerably, depending on the used milk and the method of manufacture (Sanz Sampelyao et al, 2007; Domagala et al., 2010; Markiewicz-Kęszycka et al., 2013). Most of them appear as esterified and part of them appears in a free form.

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Free fatty acids are usually released by the actions of lipases (from different sources) during lipolysis. They contribute directly to cheese flavour, particularly when they are properly balanced by products of proteolysis and by other reactions (Mallatou et al., 2003).

Besides proteins, fat and vitamins, cheese is a good source of minerals including calcium, sodium, potassium and magnesium. Cheese also contains a relatively large number of essential trace elements such as iron, iodine, copper, manganese, zinc, cobalt, selenium and chromium (Gordon, 2014). The level of minerals in cheese depends on numerous factors including those related to milk (type of milk, animal breed and period of lactation, feeding and geographical area of milk production) (Moreno-Rojas et al., 1994; Mendil, 2006), those related to the manufacturing processes and the specific variety of cheese (type of coagulation, pressing and salting conditions) (Prieto et al., 2002; Patiño et al., 2005; Anastasio et al., 2006; Mendil, 2006; González-Martín et al., 2009; Jaoude et al., 2010; Gordon, 2014) and those related to possible contamination from the equipment during process (Yüzbaşı et al., 2003; 2009). Some of minerals like Cu, Zn and Fe are essential micro nutrients and have a variety of biochemical functions in human body. But these elements can be toxic when taken in excess. Their necessity and toxicity is variable (Barać et al., 2015). In opposite, some heavy metals such as Pb and Cd present in cheese as contaminants are highly toxic, especially to children. Therefore, the levels of trace elements important for their nutritional and/or toxicological properties, in traditional dairy products such as cheeses, contribute to the characterization of the quality and adequacy of the Serbian diet.

White brined cheese usually named as “kriska cheese” is a traditional type of cheese in Serbia which is ripened and kept in brine. It can be manufactured from ovine, goat and cow milk or from any mixture of these sorts of milk. Due to different geographical areas of production, type of milk, animal breed and different autochthonous technological processes even though they belong to the same group of cheese, they have different physico-chemical, nutritive and sensory characteristics. More than 2/3 of annual production and consumption of cheese in Serbia is related to this type of cheese. However, despite the high level of production, to the best of our knowledge, there is no report on the fatty acid profiles, mineral content and heavy metal content

in those types of cheese. Thus, the aim of this work was to investigate and to compare the fatty acid profiles and the levels of trace metals and minerals in four Serbian traditional white brined cheeses. Concerning their role in the diet, comparative study of these compounds could better indicate the nutritional value of these products.

Material and methods

Cheese samples

This study covered four Serbian traditional white brined cheeses, Zlatar cheese (cow cheese), Sjenica cheeses (ovine and cow cheese), Svrlijč cheese (ovine cheese) and Homolje cheeses (ovine and cow milk). Ripened (two months old) artisanal cheeses were collected (at least three different samples of each type of cheese from the same producer) from specific geographical area in period from April to September. The collected samples were transported to the laboratory in an isothermal container, lyophilized and kept at -20 °C until analysis.

Analysis of fatty acids

Amounts of 0.5 g of lyophilized cheese was extracted in 10 mL of heptane for 1 hour in ultrasound bath and then kept at room temperature for 24 hours. The extract was filtered through a filter paper Whatman No 1 and evaporated under nitrogen steam. The lipid compounds were dissolved in 1 mL hexane and converted to fatty acid methyl esters (FAME's) according to Kostić et al (2017) by using 1 mL of 14 % BF_3/MeOH reagent. The mixture was heated at 100 °C for 1 hour, cooled to room temperature and methyl esters extracted in the hexane phase following addition of 1 mL H_2O . The samples were centrifuged for 1 min, and the upper hexane layer was removed then and concentrated under nitrogen.

FAME's were determined by capillary gas chromatography on GC instrument Agilent Technologies 6890 (USA) equipped with split/splitless injector, flame ionization detector (FID) and SP-2560 (length 100 m, i.d. 0.25 mm, film thickness 0.20 μm , Supelco, Bellefonte, USA). Injector and detector temperature were 250 °C and 260 °C, respectively. As carrier gas, helium was used at flow rate of 5 mL min^{-1} . Injected volume was 1 μL and injector split ratio was set at 20:1. The column temperature

was programmed from initial 50 °C (hold 5 min) to 240 °C (hold 20 min), with temperature rate of 4 °C min⁻¹. The total analysis time was 72.5 min. The chromatographic peaks in the samples were identified by comparing relative retention times of FAME peaks with peaks in Supelco 37 Component FAME mix standard (Supelco, Bellefonte, USA). Fatty acid content was calculated in mg g⁻¹ of lipids and expressed in relative quantities as mass % of total fatty acids.

Indexes of lipid quality

From the fatty acid profiles of cheeses the unsaturated/saturated fatty acids (SFA/UFA) ratios and desirable fatty acids (DFA) were calculated. DFA was calculated according following equation:

$$\text{DFA} = \Sigma\text{MUFA} + \Sigma\text{PUFA} + \text{C18:0}$$

Also, to relate the profile of fatty acids with the risk of cardiovascular disorders, the atherogenicity index (AI) and thrombogenicity (TI) indices were calculated, as proposed by Ulbricht and Southgate (1991) through the equation:

$$\text{AI} = [(4 \times \text{C14:0}) + \text{C16:0} + \text{C18:0}] / \Sigma\text{MUFA} + \Sigma\text{PUFA}$$

$$\text{TI} = (\text{C14:0} + \text{C16:0} + \text{C18:0}) / (0.5\text{MUFA} + 0.5\text{PUFA} - n6 + 3\text{PUFA}n3 + \text{PUFA}n3/\text{PUFA}n6)$$

AI indicates the relationship between the sum of the main saturated FAs and the main classes of unsaturated FAs. The former are considered as pro-atherogenic (favouring the adhesion of lipids to cells of the immunological and circulatory system), and the latter as anti atherogenic (inhibiting the aggregation of plaque and diminishing the levels of esterified fatty acid, cholesterol, and phospholipids, thereby preventing the appearance of micro- and macro-coronary diseases) (Prandini et al, 2011). TI expresses the tendency to form clots in the blood vessels. It is defined as the relationship between the pro-thrombogenic (saturated) and the anti-thrombogenic fatty acids (MUFAs, PUFAs - n6 and PUFAs - n3) (Garaffo et al., 2011).

Mineral profiles of Serbian traditional white cheeses in brine

The mineral content in traditional cheeses was analysed by atomic absorption spectroscopy (AAS)

(Varian Spectra AA 220). Contents of microelements Fe, Mn, Cu, Zn, Cr, Pb, Co and Cd in lyophilized cheeses were analysed after the destruction in concentrated HNO₃ and HClO₄ with the addition of 33 % H₂O₂ by wet ashing (Jonas and Case, 2001). Contents of Ca and Mg were detected after the destruction with concentrated acids HNO₃ and HCl by dry ashing (Jones and Case, 1990). Contents of P, K, and Na in lyophilized samples were determined after the destruction with concentrated acids H₂SO₄ and HClO₄ by dry ashing. Phosphorus was determined by the colorimetric method, whereas K and Na were determined by the flame-photometry method (Jones, 2001).

Statistical analysis

All measurements were done in triplicate. Data were subjected to one-way analysis of variance (ANOVA) with Microsoft Office Excel ver. 7.0 and the comparison of the mean values was done by Tuckey's test at p<0.05. Mineral contents were correlated with each other by Person two-tailed significance correlation at p<0.05 level.

Results and discussion

Fatty acids profiles of traditional Serbian white brined cheeses

Fatty acid profiles of white brined Serbian cheeses are shown in Table 1. Under experimental conditions used in this study, up to twenty one fatty acids were detected depending on the cheese variety. Twelve of them were saturated whereas up to nine were unsaturated, monounsaturated (MUFA) and polyunsaturated (PUFA) acids.

In general, fatty acid profiles of traditional white cheeses were similar qualitatively, especially regarding to saturated fatty acids. More precisely, the presence of hencosanoic acid (C21:0) in both types of Sjenica cheeses was the only qualitative difference in comparison to Homolje, Zlatar and Svrlijig cheeses. More pronounced qualitative differences can be observed in the case of unsaturated fatty acids (USFA). For example, cis-10-pentadecanoic acid (C15:1) was found only in Zlatar cheese whereas linoleic acid (C18:2n6t) was detected only in ovine cheese from Svrlijig. Such profiles were in good agreement with data reported in literature for other types of cheeses

(Domagala et al., 2009; Aguilar et al., 2014). As the cheeses were sampled during the same season (spring-summer), the absence of certain fatty acids could be attributed to initial fatty acid composition of milk, influenced by milk origin, breed, stage of lactation and animal diet (Walstra and Jenness, 1984; Zeppa et al., 2003; Sanz Sampelayo et al., 2007; Heck et al., 2009) as well as to differences in lipid metabolism of autochthonous microbial cultures (McSweeney and Sousa, 2000).

As expected, white brined cheeses like other types of cheeses are good sources of both, saturated and unsaturated fatty acids. However, SFA dominated in fatty acid profiles of all traditional white brined cheeses. Their content varied significantly ($p < 0.05$) depending on cheese variety and ranged from 65.97 % to 76.61 % (cow cheeses) and 69.68 % to 74.52 % (ovine cheese, Table 2). The lowest content of SFA was observed in Sjenica cow cheese whereas the highest ratio of these fatty acids was

in Homolje cow cheese. The most abundant saturated fatty acids in all cheeses were palmitic (C16:0) acid, stearic (C18:0) acid, and miristic (C14:0) acid. These fatty acids constituted 18.36 %-22.48 %, 9.91 %-12.31 % and 10.78 %-11.95 % of all identified fatty acids of cow cheeses, respectively. In ovine cheeses major SFA's, C16:0, C18:0, C14:0, were in the range of 18.06 %-21.11 %, 9.45 %-13.22 % and 11.78 %-12.38 %, respectively.

Based on the length of the hydrocarbon chain SFAs of cheese are usually classified as short-chain (C4-C6), medium-chain (C8-C14), and long-chain ($\geq C16$) fatty acids. According to this classification, SFAs of traditional cheeses are composed of 52.02 %-62.42 % of long chain SFAs, 4.37 %-7.38 % of short and 31.42 %-41.53 % of medium chain SFAs. As expected ovine cheeses had higher ratio of short fatty acids than cow cheeses (6.31 %-7.38 %), with the exception of Sjenica cow cheese in which short-chain SFAs represented 6.38 % of total SFAs.

Table 1. Fatty acid content of traditional Serbian white brined cheeses (%)

Saturated fatty acid (%)	White cheese in brine					
	Ovine cheeses			Cow cheeses		
	Svrljig	Homolje	Sjenica	Homolje	Sjenica	Zlatar
C4:0 butiric	2.51±0.21 ^a	2.26±0.15 ^{a,b}	2.12±0.05 ^b	1.54±0.09 ^c	2.17±0.10 ^b	1.51±0.06 ^c
C6:0 caproic	2.63±0.03 ^a	2.44±0.09 ^b	2.39±0.05 ^b	1.81±0.10 ^{c,d}	2.04±0.03 ^c	1.62±0.10 ^d
C8:0 caprylic	2.12±0.11 ^b	2.38±0.22 ^b	2.40±0.12 ^b	1.38±0.10 ^c	1.28±0.17 ^c	1.13±0.08 ^c
C10:0 capric	5.02±0.14 ^b	7.12±0.21 ^a	7.36±0.32 ^a	3.44±0.17 ^c	2.69±0.11 ^d	2.59±0.20 ^d
C12:0 lauric	3.81±0.05 ^a	4.02±0.10 ^a	4.06±0.11 ^a	3.33±0.01 ^c	2.93±0.08 ^b	3.06±0.02 ^b
C14:0 miristic	11.78±0.25 ^b	11.95±0.27 ^b	12.38±0.09 ^a	11.95±0.13 ^b	10.78±0.10 ^c	11.88±0.22 ^c
C15:0 pentadecanoic	2.78±0.04 ^d	2.94±0.07 ^c	2.84±0.10 ^c	5.34±0.23 ^a	3.05±0.06 ^c	4.0±0.16 ^b
C16:0 palmitic	21.11±0.15 ^b	18.06±0.24 ^c	18.08±0.09 ^c	20.56±0.10 ^b	18.36±0.26 ^c	22.48±0.19 ^a
C17:0 heptadecanoic	2.36±0.08 ^c	2.46±0.15 ^c	2.68±0.10 ^c	4.29±0.21 ^a	2.73±0.26 ^c	3.35±0.15 ^b
C18:0 stearic	9.45±0.21 ^f	13.22±0.24 ^a	10.05±0.10 ^d	11.06±0.16 ^c	12.31±0.22 ^b	9.91±0.31 ^{d,f}
C21:0 heneicosanoic	n.d. ^b	n.d. ^b	1.66±0.09 ^a	n.d. ^b	1.56±0.04 ^a	n.d. ^b
C22:0 behenic	6.11±0.14 ^c	7.67±0.11 ^a	3.9±0.12 ^d	1.54±0.09 ^c	6.07±0.15 ^c	6.91±0.24 ^b
Unsaturated fatty acids (%)						
C14:1 miristoleic	n.d. ^e	1.41±0.05 ^d	1.64±0.08 ^c	2.46±0.07 ^a	1.84±0.02 ^b	2.40±0.11 ^a
C15:1 cis-10-pentadecanoic	n.d. ^b	n.d. ^b	n.d. ^b	n.d. ^b	n.d. ^b	1.18±0.09 ^a
C16:1 palmitoleic	n.d. ^f	n.d.	1.16±0.10 ^d	1.56±0.05 ^c	2.04±0.07 ^b	2.59±0.10 ^a
C18:1n9c (oleic)	11.05±0.24 ^c	10.26±0.15 ^f	14.34±0.31 ^d	6.63±0.31 ^e	16.62±0.24 ^a	15.55±0.32 ^c
C18:1n9t (elaidic)	7.4±0.23 ^c	11.29±0.15 ^a	9.38±0.11 ^b	11.08±0.12 ^a	9.81±0.21 ^b	6.73±0.18 ^d
C18:2n6c linoleic	3.83±0.12 ^a	2.52±0.17 ^d	3.13±0.10 ^c	1.20±0.08 ^e	3.38±0.09 ^b	3.11±0.10 ^c
C18:2n6t linoleaidic	4.55±0.21 ^a	n.d. ^b	n.d. ^b	n.d. ^b	n.d. ^b	n.d. ^b
C18:3n6 γ -linoleic	n.d. ^c	n.d. ^c	0.43±0.03 ^a	0.46±0.02 ^a	0.34±0.01 ^b	n.d. ^c
C20:1n9 cis-11-eicosenoic	2.65±0.01 ^a	n.d. ^b	n.d. ^b	n.d. ^b	n.d. ^b	n.d. ^b

* values represent means \pm SD; values with the same letter within the same row are not statistically significant at $p > 0.05$; n.d. - not detected

Long-chain saturated fatty acids dominated in cow cheeses. Their ratio was almost identical (62.20 %-62.42 % of total SFA). Significantly ($p < 0.05$) lower ratio of these fatty acids was observed in ovine chesses (52.02 %-56.01 %).

SFAs have a poor image because there is some evidence of negative influence on blood lipids. However, despite the presence of considerable amounts of these fatty acids, there is no clear evidence relating cheese consumption to any disease. It is also known that individual SFAs influence blood cholesterol level differently (Legrand and Rioux, 2010). Total plasma cholesterol raising effects of SFAs are generally greater with medium chain lengths acids (C12:0, C14:0) than for those with longer chain lengths (C16:0 and C18:0) (German and Dillard, 2006). According to Parodi (2009) C12:0 is more potent than C14:0 and C16:0, but its ratio was only 2.93 %-3.33 % (cow cheeses) and 3.81 %-4.06 % (ovine cheeses) of all detected FAs (Table 1). It is believed that the other saturated fatty acids found in cheese neutralize their effect since they increase HDL- level (Parodi, 2009). C18:0, which is an important component of the SFAs in traditional cheeses (represented 13.56 %-18.66 % of SFAs), is rapidly converted to the MUFA oleic acid (C18:1), which is considered to be one of the healthier sources of fat in diet and is not related with cardiovascular risk (Jakobsen et al., 2009). In addition, short chain SFAs (C4-C6) and some of MSFAs (C8-C10) represented 6.85-14.27 % of all FA of traditional

cheeses. Ovine chesses had higher content of these acids than cow cheeses (12.08 %-14.27 % comparing to 6.85 %-8.18 %). These SFAs are highly digestible as they are preferentially hydrolysed from the triglycerides and are directly transferred from the intestine to the portal circulation without re-synthesis of triglycerides (Sanz Sampelayo et al., 2007). Thus, there is only a low tendency of adipose formation. These acids contribute to reducing of cholesterol level in serum and liver as well as triglyceride levels (Sanz Sampelayo et al., 2007). It has also been shown *in vivo* that butyric acid (C4:0) is a stimulant of normal colonic cell proliferation and it can also inhibit growth and proliferation of colon cancer cell lines (Aluko, 2012) whereas caprylic acid (C8:0) and capric acid (C10:0) expressed antiviral and antibacterial properties (Nair et al., 2005).

The ratio of USFAs of traditional cheeses which are composed of MUFAs and PUFAs was quite different ($p < 0.05$) and it was found to be in the range of 23.39 %-34.03 % (Table 2). The largest part of USFAs was accounted for MUFAs and among them C18:1 acid is characterized by the highest content (17.71 %-26.43 %) which is in a good agreement with data reported for milk (Markiewicz-Kęszycka et al., 2013) and other types of cheeses (Domagała et al., 2010). But, in traditional cheeses this acid existed as two geometric isomers, oleic acid (C18:1n9c) and elaidic acid (C18:1n9t) and their share in some of cheeses was quite different. While in ovine cheese from Homolje their ratio was almost

Table 2. Health lipid indices of traditional Serbian white brined cheeses*

Parameters	White cheese in brine					
	Ovine cheeses			Cow cheeses		
	Svrljig	Homolje	Sjenica	Homolje	Sjenica	Zlatar
SFA	69.68 ^c	74.52 ^b	69.92 ^c	76.61 ^a	65.97	68.44 ^d
SCSFA C4:0-C6:0	5.14 ^a	4.70 ^b	4.51 ^c	3.35 ^e	4.21 ^d	3.13 ^f
MCFA C8:0-C15:0	25.51 ^c	28.41 ^b	29.04 ^a	25.44 ^c	20.73 ^e	22.66 ^d
LCSFAC 16:0-C24:0	39.03 ^e	41.41 ^b	36.37 ^s	47.82 ^a	41.03 ^f	42.65 ^e
MUFA	18.45 ^e	22.96 ^d	26.52 ^c	21.73 ^d	30.31 ^a	28.45 ^b
PUFA	11.03 ^a	2.52 ^e	3.56 ^c	1.66 ^f	3.72 ^b	3.11 ^d
DFA	38.93 ^d	38.7 ^d	40.13 ^c	34.45 ^e	46.34 ^a	41.47 ^b
AI	2.44 ^c	2.74 ^b	2.38 ^e	3.06 ^a	1.89 ^e	2.31 ^d
TI	1.87 ^b	1.84 ^b	1.51 ^d	2.12 ^a	1.37 ^e	1.64 ^c
USFA/SFA	0.42 ^c	0.34 ^d	0.43 ^c	0.30 ^d	0.51 ^a	0.46 ^b

*data were presented as average values; values with the same letter within the same row are not statistically significant at $p > 0.05$; AI - atherogenicity index; TI - thrombogenicity index

identical, in Homolje cow cheeses elaidic acid dominated (Table 1). In other cheeses oleic acid was the most abundant MUFA.

PUFAs are significant part of identified fatty acids of investigated cheeses. Depending on the type of cheese, their ratios were 11.03 % to 1.66 % (Table 2). The highest content of these fatty acids was detected in ovine Homolje cheese due to presence of linoleic (C18:2n6t; 4.55 %) and C20:1n9 cis-11-eicosenoic acids (2.56 %). These PUFAs were not detected in other cheeses and the major polyunsaturated fatty acid in all other cheeses was linoleic (C18:2n6c). Under conditions used in this study, due to absence of standards, CLAs were not detected and quantified.

As a result of different fatty acid compositions, white brined cheeses are characterized by significantly ($p < 0.05$) different health lipid indices including index of atherogenicity (IA), index of thrombogenicity (IT), desirably fatty acids ratio (DFA) and USFA/SFA ratio (Table 2). Due to the lowest content of USFAs (23.39 %) Homolje cow cheese is characterized with the most unfavorable DFA, AI-, TI- values and USFA/SFA ratio. In opposite to this, the best health lipid indices had cow cheese from Sjenica (AI 1.89; TI 1.37 and DFA 46.34 %).

Mineral profiles of Serbian white brined cheeses

Table 3 presents the mean content of calcium, phosphorus, magnesium, potassium, sodium, and heavy metals (iron, zinc, copper, lead, cadmium, chromium, cobalt and nickel) found in traditional Serbian white cheeses. Mineral contents of these cheeses differed significantly ($p < 0.05$). Calcium and phosphorus were the most abundant in Zlatar

and Sjenica cheeses made from cow milk whereas their lowest content was registered in Sjenica ovine cheese. These results were in good agreement with data reported by González-Martín et al. (2009) but did not coincide with data reported by Raynal-Ljutovac et al. (2008) which showed that these two elements were more abundant in ovine than in cow milk. The ratio Ca:P in these cheeses was in the range of 0.7-1.33. Cow cheeses as well as Homolje ovine cheeses had this ratio in the range considered to be normal (Jennes, 1980) whereas the other cheeses had slightly lower ratios of Ca and P. Contents of K, Mg and Na also varied and were in the range of 124.5-290.4 mg/100 g, 23.20-34.78 mg/100 g and 1570-4400 mg/100 g of lyophilized cow cheese, and 124.5-265.6 mg/100 g, 24.73-31.84 mg/100 g and 1400-6220 mg/100 g of lyophilized ovine cheese, respectively. The highest content of K and Mg was observed in cow cheese from Sjenica.

Significant differences in Zn and heavy metals contents were also observed. For example, Zn content was in the range of 20.73 to 47.11 $\mu\text{g/g}$ (cow cheeses) and 16.19 to 23.45 $\mu\text{g/g}$ (ovine cheeses), whereas Fe content was 5.81-8.08 $\mu\text{g/g}$ (cow cheeses) and 2.95-9.62 $\mu\text{g/g}$ (ovine cheeses) as presented in Table 3. However, detected values were in agreement with data reported for other types of cheeses (Cichoscki et al., 2002; Herrera et al., 2006; González-Martín et al., 2009).

Pb content of investigated cheeses was approximately three to five times lower than those detected in Turkish white brined cheeses (Ayar et al., 2005, 2009) and Italian ovine cheeses (Anastasio et al., 2006). The highest level of Pb was detected in ovine cheeses from Sjenica whereas the lowest level was in ovine cheeses from Homolje. Lead presence in these

Table 3. Mineral and heavy metal content of traditional Serbian white cheeses in brine

Cheese	Ca	P	K	Na	Mg	Ca/P	Fe	Zn	Mn	Cu	Co	Pb	Cr	Ni	Cd	
	mg/100 g of lyophilized cheese						$\mu\text{g/g}$ of lyophilized cheese									
	Zlatar	1014.8 ^b	764.2 ^b	207.5 ^c	4040 ^b	26.40 ^c	1.33 ^a	6.98 ^d	27.72 ^b	0.544 ^e	0.13 ^e	1.33 ^b	0.135 ^c	0.57 ^b	/ ^c	/
Cow	Sjenica	1422.3 ^a	1375.5 ^a	290.4 ^a	1570 ^e	34.78 ^a	1.03 ^b	8.08 ^c	47.11 ^a	0.743 ^c	1.16 ^a	0.48 ^d	0.138 ^c	0.90 ^a	0.199 ^a	/
	Homolje	821.0 ^d	729.2 ^c	124.5 ^d	3650 ^c	23.20 ^d	1.12 ^c	5.81 ^e	20.73 ^d	0.668 ^d	1.01 ^a	0.85 ^c	0.058 ^s	0.66 ^a	0.25 ^a	/
	Homolje	881.5 ^c	755.4 ^b	265.6 ^b	6220 ^a	31.84 ^b	1.17 ^c	9.62 ^b	23.45 ^c	0.915 ^b	0.43 ^c	1.81 ^a	0.07 ^f	0.73 ^a	0.10 ^b	/
Ovine	Svrljig	529.3 ^f	689.9 ^d	124.5 ^d	4120 ^b	24.73 ^d	0.77 ^e	2.95 ^f	21.87 ^c	0.693 ^d	0.59 ^b	0.87 ^c	0.085 ^e	0.75 ^a	0.15 ^b	/
	Sjenica	472.4 ^e	676.8 ^d	265.6 ^b	1400 ^f	26.01 ^c	0.70 ^f	5.25 ^e	16.19 ^e	1.237 ^a	0.408 ^c	0.05 ^e	0.184 ^a	0.43 ^b	0.30 ^a	/

** values represent means of three measurements; values with the same letter within the same column are not statistically significant at $p < 0.05$

cheeses could be a result of contamination from environment during the cheese making process. Lead, due to its wide use in industrial processes, ranks as the metal of largest diffusion through the atmosphere (SEMA, 1998). This could in part explain concentrations detected in investigated cheeses produced in mountain areas of Sjenica, Homolje, Zlatar and Svrlijig which are relatively far from the urban areas and industrial plants. In addition, cadmium was not detected in investigated cheeses. The observed variations of minerals and heavy metals content could be attributed to numerous factors including type of milk, animal breed, period of lactation, feeding. Variations in technological production process (especially pressing and salting) in different production regions and among households result in different pH values of cheeses which have effect on different distribution of minerals and metals into cheese/whey or brine (Gordon, 2014).

The correlations between elements were studied and the results are shown in Table 4. The concentration of Ca was positively correlated ($p < 0.05$) with P, Mg and Zn which is in agreement with investigations of several authors (Moreno-Rojas et al., 1994; Gambelli et al., 1999; González-Martín et al., 2009). Also, Ca concentration was positively correlated with Cr concentration. In addition, González-Martín et al. (2009) found a positive correlation between concentrations of Na and P and a negative correlation between Na and Zn concentrations. In the present investigation a significant

correlation was found only between Na and Co. Iron, nickel and lead were minerals that were not correlated to other minerals in the study.

Conclusion

Results of this investigation suggest significant differences in fatty acid profiles and mineral content of Serbian traditional white cheeses in brine. The most favorable fatty acid composition and health lipid indices including index of atherogenicity, index of thrombogenicity, desirably fatty acids ratio and USFA/SFA ratio had Sjenica cheese prepared from cow milk. Sjenica cow cheese is also characterized with the highest concentration of Ca, P, K, Mg, Zn, Cu and Cr. Hence, among the investigated cheeses, Sjenica cheese had the most favorable impact on human health. This could be attributed to several factors including breed, feed, geographical position and production process. Investigated cheeses had low levels of Pb whereas absence of cadmium was detected in all cheese samples. Results of our study clearly highlighted significant importance of white brined cheese role in healthy human diet.

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Table 4. Correlation coefficients between minerals and metals of Traditional cheeses

	Ca	P	k	Na	Mg	Fe	Zn	Mn	Cu	Co	Pb	Cr	Ni
Ca	1.00	0.89*	0.48	0.09	0.79*	-0.10	0.92*	-0.21	-0.32	0.15	-0.15	0.72*	-0.07
P		1.00	0.55	-0.19	0.82*	-0.17	0.97*	-0.01	-0.14	-0.21	0.07	0.72*	0.20
K			1.00	-0.18	0.72*	0.17	0.48	0.54	0.38	-0.10	0.48	0.19	0.08
Na				1.00	0.24	-0.24	-0.08	-0.14	-0.44	0.82*	-0.67	0.41	-0.25
Mg					1.00	-0.32	0.80	0.30	0.00	0.07	0.00	0.82*	0.21
Fe						1.00	-0.17	-0.28	-0.27	0.30	0.05	-0.63	-0.59
Zn							1.00	-0.18	-0.30	-0.06	0.04	0.74*	0.04
Mn								1.00	0.86*	-0.44	0.39	0.03	0.65
Cu									1.00	-0.65	0.61	-0.24	0.55
Co										1.00	-0.62	0.09	-0.70
Pb											1.00	-0.38	0.18
Cr												1.00	0.30
Ni													1.00

*These correlation coefficients correspond to correlations that are significant at $p < 0.05$.

Profili masnih kiselina i udjeli mineralnih tvari tradicionalnih bijelih sireva Srbije

Sažetak

Istraživanje se bavi profilima masnih kiselina i udjelom mineralnih tvari tradicionalnih bijelih sireva Srbije. Istraživanja se odnose na četiri tradicionalna sira Srbije: Svrliški, Zlatarski, Sjenički i Homoljski bijeli sir koji su pripremljeni od sirovog kravljeg i ovčjeg mlijeka. Profili masnih kiselina tradicionalnih sireva bitno su različiti kako u kvalitativnom tako i u kvantitativnom smislu. Sadržaj zasićenih masnih kiselina bio je u rasponu 65,97 %-76,61 % za kravlje i 69,68 %-74,52 % za ovčje sireve. Nezasićene masne kiseline činile su 23.39 %-34.03 % (ovčji sirevi), odnosno 25.48 %-30.08 % (kravlji sirevi) identificiranih masnih kiselina. Ovisno o vrste sira, udjel masnih kiselina iznosio je 1,66 %-11,03 %. Najniži udjel zasićenih masnih kiselina utvrđen je u Sjeničkom kravljem siru. Stoga je ovaj tip tradicionalnog sira imao i najpovoljnije zdravstvene pokazatelje poput AI, (1,89), TI (1,37) i udjela poželjnih masnih kiselina (46.34 %). Također, ispitivani sirevi odlikuju se značajno različitim sadržajem mineralnih tvari. Odnos Ca:P bio je u rasponu 0,70-1,33. Najviši udjeli Ca, P, K, Mg, Zn, Cu i Cr utvrđeni su u Sjeničkom kravljem siru. Ovi sirevi nisu sadržali Cr.

Ključne riječi: bijeli sir, profil masnih kiselina, sadržaj minerala

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