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Mineral elements in milk and dairy products

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Summary

Mineral elements occur in milk and dairy products as inorganic ions and salts, as well as part of organic molecules, such as proteins, fats, carbohydrates and nucleic acids. The chemical form of mineral elements is important because it determines their absorption in the intestine and their biological utilization. The mineral composition of milk is not constant because it depends on lactation phase, nutritional status of the animal, and environmental and genetic factors. The objective of this research is to point out the research results of chemical form, content and nutritional importance of individual mineral elements that are present in various milks and dairy products.

Key words: milk, dairy products, mineral elements, nutritional significance

Introduction

On average, mineral elements account for 4 % of total body mass and part of every tissue, liquid, cell and organ in human body. There is a sufficient evidence that minerals, both independently or in proper balance with other minerals, have structural, biochemical and nutritional functions that are very important for overall human health, both mental and physical (Vahčić et al., 2010). Furthermore, they act as catalysts for many biological reactions in the body, including muscle contraction, transmission of nerve impulses and utilization of nutrients from food (Anonymous, 2010; Vahčić et al., 2010). Twenty mineral elements are assumed to be essential in human nutrition: sodium, potassium, chloride, calcium, manganese, selenium, iodine, chromium, cobalt, molybdenum, fluorine, arsenic, nickel, silicon and boron (Cashman, 2002a). Essential minerals are occasionally classified into two groups: major elements (macrominerals) and trace elements (or microminerals). The concentration of major elements (sodium, potassium, chloride, calcium, magnesium and phosphorus) in the human body exceeds 0.01 % of total body mass, whereas trace elements (remaining 14 elements) are present in much lower concentrations, and their dietary intake may be lower than 100 mg/day. All essential mineral elements can be found in milk because by definition it contains the nutrients required for growth of the young (Bates and Prentice, 1996). Milk and dairy products are an important source of dietary minerals in many European countries, accounting for 10-20 % of daily dietary intake. However, the content of major and trace elements in milk depends upon the content of these elements in soil and cattle feed, which varies considerably among and within countries (Dobrzański et. al., 2005; Malbe et al., 2010). Also, the thermal treatment of milk may have influence on mineral composition in the way that concentration of dietary minerals in consumer milk is lower than concentration in raw milk, with the exception of iron, which is higher in consumer milk (Malbe et al., 2010). On the other hand, in the study conducted by Zurera-Cosano et al. (1994) the existence of statistically significant differences were observed only for copper and iron with a tendency to decrease slightly

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during pasteurization and sterilization. In milk, mineral elements occur in several chemical forms, including inorganic ions and salts, or as parts of organic molecules such as proteins, fats, carbohydrates and nucleic acids.

The objective of this research is to present the research results that have been conducted on the chemical forms, content and nutritional importance of individual mineral elements found in various types of milk and dairy products. However, it should be emphasized that there are insufficient researches on the content and chemical form of minerals in milk and dairy products.

Chemical form and distribution of mineral elements in the soluble and colloidal milk phase

The chemical form of mineral elements found in milk and dairy products is very important due to their absorption in the intestine and biological utilization (transport, assimilation in cells and conversion into biologically active form). Of the total calcium in cow milk, 99 % is present in the skim milk fraction. Two-thirds of the total calcium can be found as calcium phosphate in the colloidal phase e.g. casein micelles or as calcium ions bound to phosphoserine (approximately one-sixth of total calcium). The remaining one-of calcium in milk can be found in the soluble phase. Ionic calcium in the soluble phase accounts for approximately 10 % of total calcium and the remaining part of soluble calcium as calcium citrate. In addition, a small quantity of calcium (0.15 %) is bound to α-lactalbumin (Cashman, 2002a). Of the total phosphorus found in cow milk, 20 % occurs as organic phosphate bound to casein, and 80 % as inorganic phosphate. Of the total content of inorganic phosphate, 44 % is bound to casein micelles as calcium phosphate and 56 % is present in the soluble phase, mostly as free phosphate ions. In cow milk, 98-100 % of magnesium is found in the skim milk fraction, 65 % of which in the soluble phase (40 % as magnesium citrate, 7 % as magnesium-phosphate and 16 % as free ions). The remaining part in the colloidal phase is bound to casein micelles (50 % to colloidal calcium phosphate and 50 % to phosphoserine in casein). The balance of salts between the soluble and the colloidal phase in cow, goat and sheep milk is important for definition of their inherent nutritional properties. Also, the balance is important for maintaining mineral elements in cheese curd during cheese production (Cashman, 2002a). In samples of goat milk, taken from different herds in the middle of lactation, the content of calcium, magnesium and phosphorus in the soluble phase was 33 %, 66 % and 39 %, respectively (Fuente et al., 1997). Also, research results of the mineral elements content in European goat breeds show that the content of soluble calcium ranges from 30 % to 38 % (O'Connor and Fox, 1977; Remeuf, 1993). Furthermore, research shows that the contents of magnesium and phosphorus in the soluble phase of goat milk are 66 % and 39 %, respectively, while the contents of calcium, magnesium and phosphorus in sheep milk in the soluble phase amounts to 21 %, 56 % and 35 % (Pellegrini et al., 1994). Most zinc in goat and sheep milk (93 % in sheep and 89 % in goat milk) and manganese (93 % in sheep and 89 % in goat milk) is present in the colloidal phase (Fuente et al., 1997). The distribution of iron and copper between the two phases of goat and sheep milk shows greater differences than other researched mineral elements. For example, the soluble phase of sheep milk contains 29 % iron and goat milk 44 %. In comparison, sheep milk contains a higher level of soluble copper (33 %) than goat milk (18 %) (Fuente et al., 1997).

Concentration of major mineral elements in various milk types and dairy products

The average concentration of major elements in goat and sheep milk is higher in relation to cow milk (except sodium), and several times higher in relation to human milk (Table 1). The concentration of major elements depends on the species, the individual animal, the method of feeding, lactation stage, and health condition of the udders (Park and Chukwu, 1988; Cashman, 2006).

Maraval and Vignon (1982) observed significant changes in the concentration of mineral elements in goat milk in the first 7 weeks of lactation. Furthermore, Khan et al. (2006) found significant influence of season and breed on the concentration of most mineral elements in sheep milk. The content of major elements in milk differs significantly from the content in blood. Compared to blood, milk contains more potassium, calcium and phosphorus, and less sodium and chloride. This is due to the sodium-potassium pump that regulates osmotic pressure

Table 1. Concentration ranges of major mineral elements in goat, sheep and cow milk compared to human milk (Posati and Orr, 1976; Jenness, 1980; Park and Chukwu, 1988; Park and Chukwu, 1989; Coni et al., 1999; Park, 2006; Deutchen Forschungsanstalt für Lebensmittelchemie, 2012)

Mineral element	Milk			
	Goat	Sheep	Cow	Human
Calcium (mg/100 g)	106-192	136-200	107-133	22-41
Phosphorus (mg/100 g)	92-148	80-145	63-102	12-17
Magnesium (mg/100 g)	10-21	8-19	9-16	3.0-3.4
Potassium (mg/100 g)	135-235	174-190	144-178	46-55
Sodium (mg/100 g)	34-50	29-31	40-58	12-15
Chloride (mg/100 g)	100-198	71-92	90-106	32-49

between the cytoplasm of blood cells and milk. At the same time, calcium is transported from the basal membrane to cytosol and onward into the Golgi apparatus of the alveolar cells of the mammary glands to be incorporated into casein micelles (Paulina and Bencini, 2004). The transport of ions, lactose and water among blood, intercellular alveolar liquids and milk is very important for osmotic balance in healthy udder, and it shows a positive correlation with the quantity of milk produced (Paulina and Bencini, 2004). There is a very high inverse level of correlation between the lactose content and the concentration of sodium and potassium in goat and other milk types (Konar et al., 1971; Park and Chukwu, 1988). Particularly high level of sodium was determined in cow colostrum. However, the sodium concentration in milk decreases to average levels a few days later. Sodium concentration in milk does not depend on its dietary intake. It is higher at the end of the lactation period, when the quantity of milk is reduced. Also, milk skimming has no effect on the sodium content (Cashman, 2002a). Unlike other mineral elements, the potassium concentration in cow colostrum is lower than in milk, but it increases over the next two to three days of the lactation period until a normal value is reached. It depends on dietary potassium intake. Research results have shown that chloride concentration is in positive correlation with potassium concentration and negative correlation with lactose content. The potassium concentration in goat milk does not depend on the lactation phase (Konar et al., 1971). The chloride concentration in colostrum is increased. However, it decreases to a normal level within two to three days. Towards end of lactation, chloride concentration increases not depending on food intake. In general, as fat content in milk increases, the content of the major minerals in milk and dairy products decreases.

Of the 20 essential mineral elements, calcium is the most common in milk (Table 1). The calcium concentration of cow milk is slightly higher in colostrum and at the end of the lactation. Removing fat from milk does not affect the magnesium content. Its content is two to three times higher in colostrum than in milk, but decreases from the first to the third day of lactation to reach its normal level (Table 1).

Table 2. Average content of major mineral elements in dried and concentrated milk in comparison with pasteurized skimmed milk (mg/100 g) (Holland et al., 1995)

Mineral element	Milk			
	Pasteurized skimmed	Dried skimmed	Evaporated	Condensed
Sodium	55	550	180	150
Potassium	150	1590	360	450
Chloride	100	1070	250	300
Calcium	120	1280	290	330
Phosphorus	95	970	260	270
Magnesium	12	130	29	33

Table 3. Average content of major mineral elements in butter, yogurt and dairy ice cream (Holland et al., 1995)

Mineral element	Dairy product (mg/100 g)		
	Butter	Yogurt	Ice cream
Sodium	750[a]	80	69
Potassium	15	280	160
Chloride	1150[a]	170	110
Calcium	15	200	130
Phosphorus	24	170	110
Magnesium	2	19	13

[a]butter to which salt was added. Butter without added salt contains 11 mg/100 g of sodium and 17 mg/100 g of chloride

The magnesium content in milk is not depending on its dietary intake (Cashman, 2002a). The content of calcium, phosphorus and magnesium in dairy products is shown in Tables 2 to 5. In general, the highest quantities of calcium and phosphorus are found in hard cheeses (Parmigiano, Gouda, Edam and Cheddar - a level up to 10 times higher than in milk). The lowest content of these elements was recorded in cream and cottage cheese. Magnesium content in cheese changes in the same way as the calcium content (Table 5).

Nutritional importance of major mineral elements present in milk and dairy products

The recommended daily allowance (RDA) of some major elements is shown in Tables 6 and 7. RDA values present the average daily calorie and nutrient intake that is considered sufficient to meet the needs of healthy infants, children and adults.

Sodium is the major cation in the extracellular fluids and is an important regulator of osmotic pressure, acid-base balance and cellular membrane potential. It is also important for the active transportation of substances through the cellular membrane. The contribution of cow milk to daily sodium intake in human nutrition is low, but cheese and some cream products which contain added quantities of salt, can provide significant sources of sodium.

Chloride is the most important extracellular anion. It is responsible for maintaining electrolyte balance. Excessive intake of table salt (sodium chloride) increases urinary calcium excretion, which negatively affects bone condition (Massey and Whiting, 1996; Cashman and Flynn, 2003). The RDA of chloride is shown in the Table 7.

Potassium is one of the most important intracellular cations. It occurs in cells in concentrations 30 times greater than in extracellular fluids. Extracellular potassium is important for the transmission of nerve impulses, muscle contractions and the maintenance of blood pressure. In addition, it has been determined that potassium intake has a positive effect on human bones. For example, the intake of alkaline potassium salts (potassium bicarbonate) by healthy adults significantly reduces urinary calcium excretion, even with excessive table salt intake (Morris et al., 1999). An adequate daily potassium intake for people is shown in Table 7. The content of sodium, potassium and chloride in milk has a physiological significance in infant nutrition. Conversely, excessive intake of these three mineral elements may cause clinical problems because they can start accumulating, limiting the renal capacity of infants (Cashman, 2002a).

Calcium accounts for 1.5-2 % of the total body mass of an adult. Of this amount, 99 % is found in bones and teeth as calcium phosphate and the remaining 1 % in extracellular fluids and intracellular structures as well as in cellular membranes.

Calcium is responsible for many regulatory functions, such as normal cardiac rhythm maintenance, blood clotting, hormone secretion, muscle contraction and enzyme activation (Cashman, 2002a). Milk and dairy products (cheese and yogurt) are very rich source of calcium (Tables 1, 3 and 4). The majority of dietary Ca (70 %) comes from dairy products because in milk, casein micelles constitute the natural vector of Ca (Canabady-Rochellea and Mellemab, 2010). The RDA for calcium (Table 6) is difficult to reach without consuming milk and dairy products. In the past, special attention

Table 4. Average content of major mineral elements in cream (Holland et al., 1995)

Mineral element (mg/100 g)	Cream						
	Fresh cream				Sour cream	Sterilized canned	UHT
	≈10 % fat	≈20 % fat	≈35-48 % fat	≈60 % fat	≈20 % fat	≈25 % fat	≈32 % fat
Sodium	49	49	37	18	41	53	33
Potassium	120	120	65	55	110	110	92
Chloride	77	80	51	40	81	78	62
Calcium	99	91	50	37	93	86	66
Phosphorus	82	76	50	40	81	73	57
Magnesium	11	9	6	5	10	10	7

was devoted to the bioavailability of calcium from milk. The average calcium absorption from cow milk varies between 21 % and 45 %. Also, the bioavailability of calcium from cheese and yogurt equals to those from milk.

Calcium absorption depends on the vitamin D level and age of a person. At the same time, it has been proven that calcium absorption in the stomach is also affected by lactose. Furthermore, the dairy products calcium bioavailability is better than of the other sources, such as vegetables. This could partly be due to their contents in highly phosphorylated fragments of caseins, named caseinophosphopeptides (CPPs). These peptides appear mainly during the elaboration of milk products such as cheese or yoghurt, under the action on caseins of milk-endogenous, milk-clotting and/or microbial enzymes. They may also arise from α_{S1}-, α_{S2}- and β-kazeina digestion in the gut (FitzGerald, 1998; Dupas et al., 2009). One unique feature of CPPs is their ability to form CPP-metal ion complexes, which would potentially increase the bioavailability of calcium and iron, notably by maintaining metals in a soluble form in the distal small intestine (Peres et al., 1999; Dupas et al., 2009). Osteoporosis is a very common disease in western countries and mostly affects women. One of its causes in old age is insufficient calcium intake when young. Maximum bone mass is achieved in the third decade of life by providing sufficient calcium intake at young age. It has also been proven that bone mass is an important factor in osteoporosis prevention (Prentice, 1997; Cashman, 2002a). Despite the data from the various calcium intervention studies, there is still considerable debate on the meaning of these effects of calcium on bone (Cashman, 2006).

Phosphorus is a major element with many important biological functions in the human body. It occurs as organic or inorganic phosphate in all body tissues and fluids, and is the main component of many biological compounds, including lipids, proteins, carbohydrates and nucleic acids (Cashman, 2002a).

Table 5. Average concentrations of major minerals in particular cheese varieties (mg/100 g) (Holland et al., 1995)

Mineral	Cheese								
	Brie	Cheddar	Cream	Cottage	Edam	Feta	Gouda	Parmigiano	Stilton
Sodium	700	670	300	380	1020	1440	910	1090	930
Potassium	100	77	160	89	97	95	91	110	130
Chloride	1060	1030	480	550	1570	2350	1440	1820	1410
Calcium	540	720	98	73	770	360	740	1200	320
Phosphorus	390	490	100	160	530	280	490	810	310
Magnesium	27	25	10	9	39	20	38	45	20

Table 6. Recommended daily allowances of calcium, magnesium and phosphorus (Institute of Medicine, 2011)

Category	Age (years)	Mineral element		
		Calcium (mg)	Magnesium (mg)	Phosphorus (mg)
Infants	0.0-0.5	200	30	100
	0.5-1.0	260	75	275
Children	1-3	700	80	460
	4-8	1000	130	500
Males	9-13	1300	240	1250
	14-18	1300	410	1250
	19-30	1000	400	700
	31-50	1000	420	700
	51-70	1200	420	700
	>70	1200	420	700
Females	9-13	1300	240	1250
	14-18	1300	360	1250
	19-30	1000	310	700
	31-50	1000	320	700
	51-70	1200	320	700
	>70	1200	320	700
Pregnancy	14-18	1300	400	1250
	19-30	1000	350	700
	31-50	1000	360	700
Lactation	14-18	1300	360	1250
	19-30	1000	310	700
	31-50	1000	320	700

Table 7. Recommended daily allowances of potassium, sodium and chloride (Institute of Medicine, 2011)

Category	Age (years)	Mineral element		
		Potassium (g)	Sodium (g)	Chloride (g)
Infants	0.0-0.5	0.4	0.12	0.18
	0.5-1.0	0.7	0.37	0.57
Children	1-3	3.0	1.0	1.5
	4-8	3.8	1.2	1.9
Males	9-13	4.5	1.5	2.3
	14-18	4.7	1.5	2.3
	19-30	4.7	1.5	2.3
	31-50	4.7	1.5	2.3
	51-70	4.7	1.3	2.0
	>70	4.7	1.2	1.8
Females	9-13	4.5	1.5	2.3
	14-18	4.7	1.5	2.3
	19-30	4.7	1.5	2.3
	31-50	4.7	1.5	2.3
	51-70	4.7	1.3	2.0
	>70	4.7	1.2	1.8
Pregnancy	14-18	4.7	1.5	2.3
	19-30	4.7	1.5	2.3
	31-50	4.7	1.5	2.3
Lactation	14-18	5.1	1.5	2.3
	19-30	5.1	1.5	2.3
	31-50	5.1	1.5	2.3

As calcium phosphate, phosphorus is the most important structural component of bones and teeth. However, excessive intake of phosphorus combined with reduced calcium intake may have negative effects on bones (Cashman, 2006). The RDA of phosphorus is shown in Table 6. Milk and dairy products are rich source of phosphorus and in western countries account for 30-45 % of the total phosphorus intake (Institute of Medicine, 2004).

Magnesium plays an important role in many physiological processes, such as metabolism of proteins and nucleic acids, neuromuscular transmission and muscle contraction, bone growth and blood pressure regulation. Magnesium is also a co-factor of many enzymes. On the other hand, magnesium deficiency may also cause osteoporosis (Rude, 1998).

There has not been much research on the bioavailability of magnesium from milk for the human body in human nutrition. Studies of metabolic balance have shown that 16-43 % of magnesium is absorbed from infant formulas based on cow milk, and that lactose facilitates magnesium absorption. In western countries 16-21 % of total magnesium is consumed through milk and dairy products (Cashman, 2002a).

Concentration of trace elements in milk and dairy products

Unlike the major elements, trace elements are present in the human body in the concentrations lower than 0.01 % of the total body mass. Of the 20 essential minerals, 14 are trace elements: iron, copper, zinc, manganese, selenium, iodine, chromium, cobalt, molybdenum, fluorine, arsenic, nickel, silicon and boron. Scientific researches on test animals have proven that some of the above elements (arsenic, nickel, silicon and boron) are essential. Therefore, it is assumed that they are also essential for humans (Cashman, 2002b). Many other trace elements also occur in milk. However, they are not nutritionally important. These include lithium, bromine, aluminium, strontium, silver, lead, tin, vanadium, mercury, cadmium, rubidium and caesium.

Many of the trace mineral elements are toxic. However, their concentrations in milk are too low to pose a threat to human health. Like content of other minerals present in milk, the concentration of trace elements (Table 1 and 8) is not constant. It depends on the lactation stage, nutritional status of the animal, and environmental and genetic factors (Cashman, 2002b). The content of trace elements

Table 8. Concentrations of trace elements in goat, sheep and cow milk compared to human milk (Posati and Orr, 1976; Jenness, 1980; Park and Chukwu, 1988; Park and Chukwu, 1989; Flynn and Cashman, 1997; Coni et al., 1999; Park, 2006; Deutchen Forschungsanstalt für Lebensmittelchemie, 2012)

Mineral element	Milk			
	Goat	Sheep	Cow	Human
Sulphur (mg/100 g)	28	29	32	14
Iron (μg/100 g)	36-75	62-100	30-70	26-58
Copper (μg/100 g)	11	11-88	2-30	22-77
Manganese (μg /100 g)	5.5	5.3	1.3-4.0	700ng
Zinc (μg/100 g)	242	415	74-145	0.38
Iodide (μg/100 g)	2.1-11	2.0	2.0-6.0	0.5-9.0
Selenium (μg/100 g)	0.7	0,9	1.3-1.7	1.0-5.3
Fluoride (μg/100 g)	-	-	11-21	13-25
Cobalt (ng/100 g)	270	360	50-130	114
Nickel (μg/100 g)	0.3-19	5,4	0.4-6.0	0.4-3.0
Molybdenum (μg/100 g)	-	-	2.4-6.0	1.0
Boron (μg/100 g)	-	-	19-95	-
Bromide (μg/100 g)	411-503	-	154-293	100
Chromium (μg/100 g)	0.5-15	0,32	1.0-4.0	4.1
Nitrate (μg/100 g)	-	-	20-1240	-
Aluminium (μg/100 g)	15	51	46	0.06

- no data

in goat and other milk types also depends on the species, its individual characteristics, feeding method, lactation stage, and health condition of udder (Park and Chukwu, 1989). Sheep milk contains approximately 0.9 % ash, compared to 0.7 % in cow milk (Park et al., 2007). A conclusion may be that the content of minerals in sheep milk is higher than in cow milk, primarily due to differences in nutrition and metabolism (Rincon et al., 1994). To date, there has been little research on trace elements in sheep milk, although they could play an important role due to their possibly positive influence on human health. By carrying out discriminatory analysis of the mineral composition in 360 samples of raw milk, (120 samples of cow, goat and sheep) statistical distance and significant differences were established in 120 samples of cow milk compared to 120 samples of goat milk, while in 10 % of the cases there was a correspondence between the samples of goat and sheep milk (Jay, 2000). These results clearly show a separation of elements in terms of the milk (Jay, 2000; Haenlein and Wendorff, 2006).

Increased exposure of dairy animals to growing environmental pollution has also increased the need for more research regarding the content of heavy metals in milk. Heavy metals, such as lead and platinum, which can be found in exhaust gases, can be absorbed when animals graze near major transportation routes (Ikeda et al., 1996; Raghunath et al., 1997). In addition, negative effects of lead and cadmium on human health were detected. Trace elements like copper and zinc are essential and have a role in many biological functions (Tripathi et al., 1999). However, if present at higher levels, they can have negative effects on human health (Brewer, 2010). Research results show that the consumption of sheep milk products in Italy leads to an intake of 15 % of the permissible content of heavy metals (Coni et al., 1999). The content of cadmium, which is also a heavy metal, is significantly higher in sheep milk than in cow milk, probably due to differences in nutrition and metabolism between two species (Coni et al., 1999; Haenlein and Wendorff, 2006; Herwig et al., 2011).

Research on other trace elements shows that, for example, the iron concentration in milk is reduced by 35 to 50 % in the first three days of lactation; after that it remains at a constant level, and it does not depend on nutrition. Furthermore, 14 % of the total iron content in milk can be found in milk fat bound to the membrane of fat globules; 24 % is bound to casein (probably to phosphoserine); 29 % is linked to whey proteins, while 32 % is bound to low molecular mass compounds (Cashman, 2002b). Bioavailability of iron from human milk ranges from 49 to 70 %, which is significantly higher than from cow milk (10 to 34 %). There is no clear explanation for this difference. However, it might be explained by the high level of lactoferrin (glycoprotein that binds iron ions) present in human milk. Another possible explanation may be found in the high content of lactose and ascorbate in human milk, which facilitates iron absorption, and in low content of proteins, calcium and phosphorus, which inhibit absorption (Cashman, 2002b).

The average zinc concentration in milk is 3.9 mg/L (Flynn and Cashman, 1997). However, it should be noted that there are great variations in concentration (2.0 to 6.0 mg/L). Zinc in cow colostrum is reduced by 50 % in the first three days of lactation after that further change is negligible. Hard sheep cheeses are rich source of zinc (Samaržija et al., 2005) due to inherent high concentration in sheep's milk (Table 1). Zinc in nutrition also increases its content in milk. In addition, it was determined that addition of zinc to milk results in reduced somatic cell count (Pechovà et al., 2006). Only 1 to 3 % of zinc in milk is related to the lipid fraction, while the remaining part can be found in the skim milk fraction. Also, out of the total zinc content present in the skim milk fraction, 95 % is bound to phosphoserine by casein micelles and 5 % to citrate. The bioavailability of zinc in human milk is much higher than in cow milk, because in human milk it is bound to ligands of low molecular mass (for example, citrate), which facilitates absorption. Also, the binding of a large proportion of zinc to casein in cow milk (10 times higher than in human milk), may cause it to be blocked within the casein curd that is produced in the abdomen, making it unavailable for absorption (Pabón and Lönnerdal, 2000). Contrary, research conducted on rats established a high capacity for zinc absorption (85 to 95 %) from human and cow milk, and dairy infant formula. It is possible that the low concentration of zinc in human milk contributes to better absorption because it is homeostatically controlled, and small quantities are better absorbed than large (Cashman, 2002b).

The concentration of copper in milk is also reduced by 50 % in the first three days of lactation, but unlike iron and zinc, addition of copper to animal feed increases its content in milk. There is little information on the content of absorbed copper in the human body. Experiments on rats showed 83 % absorption from human milk, 76 % from cow milk, and 86 to 87 % from dairy infant formula (Cashman, 2002b).

Manganese content is higher in colostrum (100 to 160 μg/L) than in milk (20 to 50 μg/L), reduced by more then 50 % in the first three days of lactation. In cow milk 67 % of the manganese is bound to casein, 1 % to globular fat membranes, 14 % to whey proteins, and 18 % to low molecular weight fraction. Research results show that manganese absorption from human milk in healthy adults amounts to 8.2±2.9 % and is significantly higher than from cow milk (2.4±1.7 %), while manganese absorption from dairy infant formula amounted to 1.7±5.9 %. Nevertheless, the absolute content of the absorbed manganese from dairy infant formula and cow milk was higher than from human milk because of its higher inherent concentration in those types of milk. On the other hand, studies conducted on rats did not show any significant differences in absorbed manganese from human and cow milk and, also dairy infant formula (Cashman, 2002b).

Selenium in plants is affected by the content and availability of the element in soil while selenium content of milk is affected by the selenium content in feeds and its availability (Reykdal et al., 2011). Also, processing of milk can diminish selenium concentration (Navarro-Alarcon and Cabrera-Vique, 2008). Selenium is linked to the enzyme glutathione peroxidase (12 % of the total content). Less than 0.1 % of total selenium content is bound to fat (Cashman, 2002b).

The iodine content depends on the season and dietary intake; it varies from 20 to >4000 μg/L. The most of iodine in milk (80 to 90 %) is found in inorganic form; another 5 to 13 % is bound to proteins by covalent bond or weak intermolecular bonds (Cashman, 2002b).

The chemical form of chromium in milk is not known, although it mostly occurs in triple bond form. The average content of chromium and cobalt in milk depends on their dietary intake.

Molybdenum content in milk is bound to xanthine oxidase and is dependent on feed. Average fluorine content in milk is 20 μg/L (ranging from 10 to 140 μg/L). Approximately 46 to 64 % of fluorine content in milk is present as free ion, the remaining is bound to proteins (Cashman, 2002b). Little is known about the chemical forms of cobalt, arsenic, nickel, silicon and boron in milk. The amounts of these elements in milk and dairy products are shown in Tables 8 to 12.

Little research is available on the effects of the lactation stage, nutritional status, and environmental and genetic factors on the content of these elements.

Nutritional importance of trace elements present in milk and dairy products

As with major elements, the best way to determine the nutritional importance of trace elements is

Table 9. Average concentration of some trace elements in concentrated milk (Holland et al., 1995)

Trace element	Milk			
	Pasteurized skimmed	Powdered skimmed	Evaporated	Condensed
Iron (mg/100 g)	0.05	0.27	0.26	0.23
Copper (mg/100 g)	traces	traces	0.02	traces
Zinc (mg/100 g)	0.4	4.0	0.9	1.0
Manganese (mg/100 g)	traces	traces	traces	traces
Selenium (μg/100 g)	1.0	11	3.0	3.0
Iodine (μg/100 g)	15	150	11	74

to compare their content in milk and dairy products (Tables 8 to 12) with the recommended daily allowance (Table 13).

Iron as an essential trace element participates as catalyst in several metabolic reactions. As a component of hemoglobin, myoglobin, citochrome and other proteins, iron plays an important role in the transport, storage and utilisation of oxygen. It is also a co-factor of many enzymes (Bates and Prentice, 1996). Milk and dairy products are poor source of iron. Iron deficiency in the human body is one of the most common health issues, occurring in infants and children because of fast growth and low dietary intake. This problem can be prevented by addition of iron to dairy infant formulas since additional ascorbate in infant formulas improves iron absorption (Bermejo et al., 2002).

Zinc is very important for growth, sexual development, the healing of wounds as well as normal functioning of the immune system and other physiological processes. Zinc is a component of the hormone insulin. It assists in the functioning of several other hormones that are important for reproduction and synthesis of DNA, RNA and proteins (Salgueiro et al., 2002). It is also a co-factor of many enzymes that are included in most of metabolic processes. Dairy products such as milk, cheese and yoghurt are very important in human nutrition, but an insufficient source of zinc. It is estimated that in western countries the contribution of dairy products to the total zinc intake ranges from 19 to 31 % (Cashman, 2002b).

Copper is essential element important for the absorption of iron and as cofactor of enzymesin glucose metabolism and synthesis of hemoglobin, connective tissues and phospholipids (Solaiman et al., 2001). Copper deficiency in the human body is very rare, occurring only in cases of long-term starvation. Milk and dairy products are a poor source of copper (Davis and Mertz, 1987) (Tablica 9).

Manganese is a specific enzyme co-factor involved in the synthesis of mucopolysaccharides, and a non-specific co-factor for many other enzymes. There are several known manganese metaloenzymes like arginase, glutamine synthetase, phosphoenlopyruvate decarboxilase and manganese superoxide dismutase (Aschner and Aschner, 1991). Manganese can be found in significant quantities in all foodstuffs. Its deficiency has not been recorded as a cause of disturbance or disease. Cow milk is a poor source of manganese. Its contribution to the total manganese intake in western countries is low (1 to 3 %). Of the total dietary intake of manganese only 3 to 5 % are successfully absorbed. The remaining quantities are eliminated from the body through faeces (Au et al., 2008).

Selenium is the main component of the enzyme glutathione peroxidase, which is present in many types of tissues. In combination with vitamin E, catalase and superoxide dismutase, it acts as an antioxidant (Somer and Ínam, 2000). After dietary intake, selenium is converted into organic form, mostly as seleno-methionine, which is then incorporated into proteins (Petrera et al., 2009). In some

Table 10. Average concentrations of some trace elements in cream (Holland et al., 1995)

	Content in 100 g of cream						
	Fresh cream				Sour cream	Sterilized canned	UHT
Trace element	≈10 % fat	≈20 % fat	≈35-48 % fat	≈60 % fat	≈20 % fat	≈25 % fat	≈32 % fat
Iron (mg)	0.1	0.1	0.2	0.1	0.4	0.8	1.0
Copper (mg)	traces	traces	traces	0,09	traces	traces	traces
Zinc (mg)	0.3	0.5	0.2	0.2	0.5	1.1	0.4
Manganese (mg)	traces	traces	traces	traces	traces	traces	traces
Selenium (μg)	traces	traces	traces	traces	traces	traces	traces

Table 11. Average content of some trace elements in butter, yogurt and dairy ice cream (Holland et al., 1995)

Trace element	Content in 100 g of product		
	Butter	Yoghurt	Dairy ice cream
Iron (mg)	0.2	0.1	0.1
Copper (mg)	0.03	traces	0.02
Zinc (mg)	0.1	0.7	0.3
Manganese (mg)	traces	traces	traces
Selenium (μg)	traces	2.0	1.5
Iodine (μg)	38	63	-

Table 12. Average content of some trace elements in some cheese types (Holland et al., 1995)

Trace element	Content in 100 g of cheese								
	Brie	Cheddar	Cream	Cottage	Edam	Feta	Gouda	Parmigiano	Stilton
Iron (mg)	0.8	0.3	0.1	0.1	0.4	0.2	0.1	1.1	0.3
Copper (mg)	traces	0.03	0.04	0.04	0.05	0.07	traces	0.33	0.18
Zinc (mg)	2.2	2.3	0.5	0.6	2.2	0.9	1.8	5.3	2.5
Manganese (mg)	traces	traces	traces	traces	traces	traces	traces	0,1	traces
Selenium (μg)	3.6[a]	12	1.0	4.0	6.4[a]	5.0[a]	8.0[a]	11	11

areas of China with low selenium concentrations in the soil there are many cases of the Keshan disease caused by selenium deficiency.

Low selenium concentrations in the human body have also been observed in New Zealand and Finland, countries with low selenium concentrations in the soil. The RDA of selenium is shown in the Table 13.

Iodine is an essential component of thyroid hormones that are important for the control of basal metabolism and reproduction. Iodine deficiency in the human organism can result in enlargement of the thyroid gland. On the other hand, a high concentration of dietary iodine can lead to a slowdown in thyroid gland function (Reid et al., 2008; Soriguer et al., 2010). Iodine is the only trace element that is considered to be excessively present in milk, due in part to the excessive use of organic iodide salts and iodophor for disinfection. The RDA for iodine is shown in Table 13. The contribution of milk and dairy products to total iodine intake ranges from 6 to 7 % in Germany to 37 % in Great Britain (Schöne et al., 2009).

Molybdenum is also an essential component of several enzymes, including xanthine oxide reductase, aldehyde oxidase and sulphite oxidase, where it occurs as prosthetic group of molybdopterin (Hille et al., 2010). It is not known whether the human body needs molybdenum as such or as molybdopterin.

The RDA of molybdenum is shown in Table 13. Milk contributes significantly to total molybdenum intake - as much as 36 % in western countries (Cashman, 2002b; Yoshida et al., 2006.).

It is assumed that chromium is an essential nutrient in human nutrition. Lack of chromium can cause problems with lactose tolerance. Cobalt is the component of vitamin B_{12}, which is its only known function. Fluorine is accumulated in hard tissues, such as bones and teeth, and although it is not an essential element, it is considered important because it prevents tooth decay. There are no RDAs because limiting factor has not been determined. Its nutritional function is not yet known. Arsenic, nickel, silicon, and boron are essential elements in animals, so it can be assumed that this is also the case with the human body (Casey et al., 1995). The nutri-

Table 13. Recommended daily allowances of particular trace elements (Institute of Medicine, 2011)

		Trace elements									
Category	Age (Years)	Iron (mg)	Zinc (mg)	Iodine (μg)	Selenium (μg)	Copper (μg)	Manganese (mg)	Fluoride (mg)	Chromium (μg)	Molybdenum (μg)
Infants	0,0-0,5	0.27	2	110	15	200	0.003	0.01	0.2	2
	0,5-1,0	11	3	130	20	220	0.6	0.5	5.5	3
Children	1-3	7	3	90	20	340	1.2	0.7	11	17
	4-8	10	5	90	30	440	1.5	1	15	22
Males	9-13	8	8	120	40	700	1.9	2	25	34
	14-18	11	11	150	55	890	2.2	3	35	43
	19-30	8	11	150	55	900	2.3	4	35	45
	31-50	8	11	150	55	900	2.3	4	35	45
	51-70	8	11	150	55	900	2.3	4	30	45
	>70	8	11	150	55	900	2.3	4	30	45
Females	9-13	8	8	120	40	700	1.6	2	21	34
	14-18	15	9	150	55	890	1.6	3	24	43
	19-30	18	8	150	55	900	1.8	3	25	45
	31-50	18	8	150	55	900	1.8	3	25	45
	51-70	8	8	150	55	900	1.8	3	20	45
	>70	8	8	150	55	900	1.8	3	20	45
Pregnancy	14-18	27	12	220	60	1000	2.0	3	29	50
	19-30	27	11	220	60	1000	2.0	3	30	50
	31-50	27	11	220	60	1000	2.0	3	30	50
Lactation	14-18	10	13	290	70	1300	2.6	3	44	50
	19-30	9	12	290	70	1300	2.6	3	45	50
	31-50	9	12	290	70	1300	2.6	3	45	50

tional functions of these elements are still unknown and their RDAs have not yet been defined. Milk and dairy products do not provide a significant contribution to their total intake, except for chromium (21 %) and nickel (11 %) (Cashman, 2002b).

Conclusion

Although the subject is very important there are no many recently published papers which are dealing with minerals in milk and dairy products. Essential mineral elements, including sodium, potassium, chloride, calcium, manganese, selenium, iodine, chromium, cobalt, molybdenum, fluorine, arsenic, nickel, silicon and boron, can be found in all milk types and dairy products. They are present in the form of inorganic ions and salts, or are part of organic molecules like proteins, fats, carbohydrates and nucleic acid. Sodium, potassium, chloride and iodine can be found in milk and infant formulas in a chemical form which allows an almost entire absorption in the human body. The bioavailability of calcium and magnesium has not yet been sufficiently researched. Among sheep, goat and cow milk the bioavailability of iron and zinc from cow milk is the highest, however, significantly lower than in human milk. Very little information is available on the bioavailability of copper, manganese, selenium, fluorine and other trace elements present in milk and dairy products. However, it is assumed that lactose, ascorbate, citrate, phosphopeptides and lactoferrin have a significant impact on the absorption of mineral elements. Furthermore, milk does not contain substances such as phitates and polyphenols, which strongly inhibit the absorption of minerals in human body.

Mineralni sastav mlijeka i mliječnih proizvoda

Sažetak

Mineralni elementi se u mlijeku i mliječnim proizvodima nalaze u obliku anorganskih iona i soli, ili kao dio organskih molekula kao što su bjelančevine, masti, ugljikohidrati i nukleinske kiseline. Kemijska forma u kojoj su mineralni elementi prisutni je vrlo važna jer o njoj ovisi apsorpcija u želucu i time njihovo biološko iskorištenje. Mineralni sastav mlijeka nije konstantan i ovisi o stadiju laktacije, hranidbenom statusu životinje, okolišnim uvjetima i genetskim čimbenicima. Cilj ovog rada je prikazati dosadašnje rezultate istraživanja koncentracija, kemijske forme i prehrambene važnosti pojedinih mineralnih elemenata koji su prisutni u različitim vrstama mlijeka i mliječnih proizvoda.

Ključne riječi: mlijeko, mliječni proizvodi, mineralni elementi, prehrambena važnost

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