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Review

Milk and Dairy Products: A Unique Micronutrient Combination

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Key words: milk, dairy products, minerals, vitamins, nutrition, health

Milk and dairy products contain micronutrients such as minerals and vitamins, which contribute to multiple and different vital functions in the organism. The mineral fraction is composed of macroelements (Ca, Mg, Na, K, P, and Cl) and oligoelements (Fe, Cu, Zn, and Se). From a physicochemical point of view, the chemical forms, the associations with other ions or organic molecules, and the location of macroelements such as Ca, Mg, Na, K, P, and Cl in milk are relatively well described and understood. Thus, it is admitted that these macroelements are differently distributed into aqueous and micellar phases of milk, depending on their nature. K, Na, and Cl ions are essentially in the aqueous phase, whereas Ca, P, and Mg are partly bound to the casein micelles. About one third of the Ca, half of the P, and two thirds of the Mg are located in the aqueous phase of milk. Dairy products are more or less rich in these different minerals. In cheeses, mineral content depends mainly on their processing. The Ca content is strongly related to the acidification step. Moreover, if acidification is associated with the draining step, the Ca content in the cheese will be reduced. Thus, the Ca content varies in the following increasing order: milks/fermented milks/fresh cheeses < soft cheeses < semi-hard cheeses < hard cheeses. The chemical forms and associations are less described than those present in milk. Concerning Ca, the formation of insoluble calcium phosphate, carbonate, and lactate is reported in some ripened cheeses. The NaCl content in cheeses depends on the salting of the curd. From a nutritional point of view, it is largely admitted that milk and dairy products are important sources of Ca, Mg, Zn, and Se. The vitamin fraction of milk and dairy products is composed of lipophilic (A, D, E, and K) and hydrophilic (B_1, B_2, B_3, B_5, B_6, B_8, B_9, B_{12}, and C) vitamins. Because of their hydrophobic properties, the lipophilic vitamins are mainly in the milk fat fraction (cream, butter). The hydrophilic vitamins are in the aqueous phase of milk. For one part of these vitamins, the concentrations described in the literature are not always homogenous and sometimes not in accordance between them; these discrepancies are due to the difficulty of the sample preparation and the use of appropriate methods for their quantification. However, there is no doubt of the significant contribution of milk and dairy products to the intake of vitamins. Milk and dairy are considered essential sources for vitamins.

Key teaching points:

- Milk and dairy products are unique micronutrient combinations with recognized health benefits.
- The concentration, chemical forms, and location of different minerals are relatively well known and described. For example, Ca is present in dairy products in different forms: free, associated with citrate, inorganic and organic phosphates, and free fatty acids.
- Milk and dairy products are excellent sources of Ca, P, Mg, Zn, and Se.
- The concentration of vitamins in milk and dairy products is variable and depends on several factors such as biosynthesis, animal feeding, physicochemical conditions (heat, light, O_2, oxidant agents), and analytical methods for their determinations.
- Vitamins A, D, E, and K are mainly located in the lipid phase and vitamins of group B and C in the aqueous phase.
- Milk and dairy products are excellent sources of vitamins A, B_1, B_2, and B_{12}.

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INTRODUCTION

Milk and dairy products provide macronutrients (proteins, lipids, and fat) that contribute to their nutritive and biological values. They contain also micronutrients represented by minerals and vitamins. These compounds, not synthesized by the human body, are not sources of energy but contribute to different vital functions (Table 1). The mineral fraction in milk and dairy products is made up of macroelements (Ca, Mg, Na, K, P, and Cl) and microelements (Fe, Cu, Zn, and Se). Vitamin fraction is composed of lipophilic (A, D, E, and K) and hydrophilic (B_1, B_2, B_3, B_5, B_6, B_8, B_9, B_{12}, and C) vitamins. Most of them are synthesized by plants and microorganisms.

Today, the analytical methods of quantification of these micronutrients are efficient and allow us to have a precise idea of the contents of these micronutrients in milk but also in different dairy products [1–7]. This knowledge is important in dairy science and technology to understand the structural organization of milk and the properties of dairy products in terms of texture, organoleptic properties, and stability but also nutrition.

The objective of this review is to describe the actual knowledge of these compounds in milk and dairy products. Special attention is paid to the concentration, location, and chemical forms of these compounds. This knowledge could be useful to explain some relationships with the observed effect on health.

MINERALS OF MILK AND DAIRY PRODUCTS

Calcium (Ca)

Ca is one of the major minerals present in milk and dairy products. In cow milk, its concentration is about 1200 mg/L. In this milk, 99% of the Ca is in the skim milk, where it is

Table 1. Biological and Physiological Roles of the Micronutrients Present in Milk and Dairy Products

Macroelements	
Calcium	Bone and teeth acquisition and maintenance; blood pressure; muscle contraction; blood clotting; cofactor of enzymatic systems; obesity
Phosphorus	Bone and teeth acquisition and maintenance; blood pH; component of biological molecules (RNA, DNA, phospholipids, ATP); metabolism
Magnesium	Cofactor of enzymatic systems; phosphorylation; DNA transcription; protein synthesis; neuromuscular transmission; muscle contraction
Sodium	Blood pressure; muscle contraction; ionic equilibrium
Potassium	Blood pressure; muscle contraction; ionic equilibrium
Chloride	Blood pressure; muscle contraction; ionic equilibrium
Oligoelements	
Iron	Component of heme in hemoglobin, myoglobin, cytochromes, cofactor of enzymatic systems
Zinc	Cofactor of enzymatic systems playing roles in the DNA, RNA, and proteins synthesis; component of insulin
Copper	Cofactor of enzymatic systems; role in respiratory chain (cytochrome C oxidase); catabolism of dopamine
Selenium	Cofactor of enzymatic systems (glutathione peroxidase); antioxidant
Lipophilic vitamins	
Vitamin A	Antioxidant; skin health; vision; reproduction; immunity; growth; gene regulation
Vitamin D	Regulation of calcium availability
Vitamin E	Antioxidant; cell membrane integrity; immunity
Vitamin K	Homeostasis of calcium; blood clotting; inhibition of apoptosis; antioxidant; cofactor of γ-glutamyl-carboxylase
Hydrophilic vitamins	
Vitamin B_1 (thiamin)	Cofactor of enzymes implicated in the cellular energetic metabolism
Vitamin B_2 (riboflavin)	Antioxidant; prosthetic group of enzymes, oxidation-reduction reactions; cellular respiration; energy metabolism; cellular antioxidant, metabolisms of lipids, nucleic bases, and amino acids
Vitamin B_3 (niacin)	Cellular respiration; energy metabolism; cellular antioxidant; metabolisms of lipids, nucleic bases, and pentose sugars
Vitamin B_5 (pantothenic acid)	Constituent of coenzyme A; cellular respiration; energetic metabolism; metabolisms of lipids, nucleic bases, and amino acids, transmission of nervous signal; transport of blood gas
Vitamin B_6 (pyridoxal)	Amino acids metabolism; transport of blood gas; activation of other vitamins (B_9 and B_3)
Vitamin B_8 (biotin)	Prosthetic group of several enzymes; energy metabolism; metabolisms of lipids, amino acids, other vitamins (B_9 and B_{12}); regulation of gene expression
Vitamin B_9 (folate)	Hematopoiesis; synthesis of nucleic bases; metabolism of monocarbon groups
Vitamin B_{12} (cobalamines)	Vitamin B_9 metabolism; hematopoiesis; energy metabolism
Vitamin C (ascorbic acid)	Antioxidant; cofactor of enzyme; metabolism of amino acids; synthesis of hormones and neurotransmitters

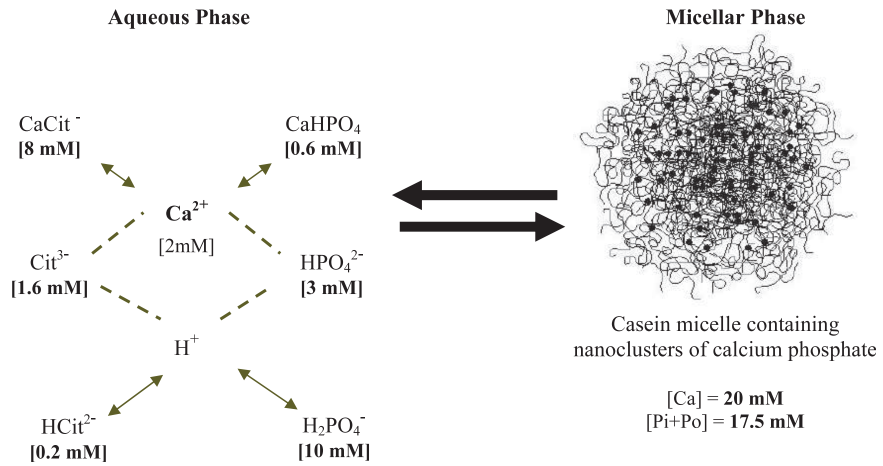

Fig. 1. Calcium and phosphate distributions in milk at pH 6.7. In the aqueous phase, calcium is free and associated to inorganic phosphate and citrate. In the micellar phase, calcium is associated with organic phosphate Po (phosphoseryl residues in casein molecules) and inorganic phosphate (Pi) to form nanoclusters (black points in the interior of casein micelles). The concentrations of the different associations are indicated in brackets.

distributed between the micellar (about 800 mg/L) and aqueous phase (about 400 mg/L; Fig. 1). In the aqueous phase, Ca is free (ionic calcium Ca^{2+}) and associated to citrate and inorganic phosphate (Pi) to form the corresponding salts. The aqueous phase is considered to be saturated in calcium phosphate. In this aqueous phase, Ca is also associated with whey proteins such as α-lactalbumin and osteopontin. In the micellar phase, Ca is associated with organic Po (phosphoseryl residues of casein molecules) and Pi. In casein micelles, these associations between Ca and phosphate form granules named nanoclusters. These mineral structures have a diameter close to 3 nm [8–11]. Today, their exact chemical composition is not well known.

There is a thermodynamic equilibrium between the aqueous and micellar phases that is relatively well described and theoretically calculated [12,13]. The Ca and Pi present in one phase can be transferred to the other phase depending on the physicochemical conditions of milk. The intensity of these modifications between these 2 phases, named "mineral equilibrium of milk," depends on the physicochemical conditions [14,15]. One of the most important modifications commonly performed is the biological acidification (fermentation of lactose in lactic acid). Thus, during this step, Ca is solubilized and transferred to the aqueous phase of acidified milk [13–17]. In some cases, the aqueous phase is removed and some dairy products such as cheeses have different calcium concentrations. As shown in Table 2, Ca content varies in the following increasing order: milks/fermented milks/fresh cheeses < soft cheeses < semi-hard cheeses < hard cheeses. The concentrations can be higher than 1000 mg/100 g of product in some cheeses, such as parmesan (Table 2).

Other considerations concerning Ca are its location and form in dairy products. Thus, in acidified dairy products such as fermented milks with pH close to 4.6, Ca is mainly free in the ionic form (Ca^{2+}). In ripened cheeses (Camembert, Cheddar, and Emmental), Ca can exist in different chemical and physical forms of precipitates of calcium phosphate, calcium lactate, and calcium carbonate [18–23]. The presence of phosphopeptides and free fatty acids was also determined in ripened cheeses, and these molecules can bind Ca to form phosphopeptide-Ca complexes and soap, respectively.

The recommended dietary allowance for Ca is about 800 to 900 mg for adults, 1000 mg for pregnant and lactating women, and 1200 mg for adolescents and elderly persons. From these recommendations, milk and dairy products are important sources of Ca; 600 ml of milk corresponds to 720 mg of Ca (i.e., 60%–80% of the recommended dietary allowance). Thus, dairy products contribute about 70% of Ca to the human diet [1,2,24]. With the aim to increase the Ca concentration in milk and dairy products, different studies are in progress [14,25,26].

Phosphorus (P)

P is also an important element present in milk and dairy products (Table 1). In milk, its concentration expressed in total P is about 950 mg/L. In terms of the chemical form, its description is complex because different forms of P exist. Schematically, P exists under organic and inorganic phosphates (Po and Pi, respectively). Po is phosphate bound to organic molecules such as casein molecules (phosphorylation of serine to form phosphoseryl residues), phospholipids, RNA, DNA, nucleosides, nucleotides, and sugar phosphate. Pi corresponds to a phosphate ion, which can be differently ionized depending on the pH value. At the pH of milk (about 6.7), there is an acido-basic equilibrium between the forms HPO_4^{2-} and $H_2PO_4^{-}$. Another complexity with this description is the various locations of these different forms of P. In milk, Po is mainly associated with casein molecules, which are in the micellar phase. The other forms of Po (phospholipids, RNA,

Table 2. Concentrations of Minerals in Some Dairy Products [7], Expressed in Milligrams for 100 g of Product

	Mineral							
	Ca	P	Mg	Na	K	Fe	Zn	Cu
Blue (USA)	528	387	23	1395	256	0.3	2.7	0.04
Brick	674	451	24	560	136	0.43	2.6	0.024
Brie	184	188	20	629	152	0.5	2.4	0.019
Camembert	387	346	20	842	187	0.33	2.4	0.021
Cheddar	721	512	28	620	98	0.68	3.1	0.031
Cheshire	643	464	21	700	95	0.21	2.8	0.042
Cottage	60	132	5	405	84	0.14	0.4	0.028
Cream	80	104	6	295	119	1.2	0.5	0.016
Edam	731	535	30	965	188	0.44	3.7	0.036
Feta	492	337	19	1116	62	0.65	2.9	0.032
Gouda	700	546	29	819	120	0.24	3.9	0.036
Gruyere	1011	605	36	336	81	0.17	3.9	0.032
Limburger	498	393	21	800	128	0.13	2.1	0.021
Mozzarella (whole milk)	517	371	19	373	67	0.18	2.2	0.02
Munster	717	468	27	628	134	0.41	2.8	0.031
Neufchatel	75	136	7	399	114	0.28	0.5	0.016
Parmesan (grated)	1376	807	51	1861	107	0.95	3.2	0.037
Pasteurized processed cheese	723	526	28	1552	284	0.6	3.5	0.03
Port salut	650	360	24	534	136	0.43	2.6	0.022
Provolone	756	496	28	875	138	0.52	3.2	0.026
Ricotta (whole milk)	207	158	11	84	105	0.38	1.2	0.021
Roquefort	662	392	30	1809	91	0.56	2.1	0.034
Tilsit	700	500	13	753	64	0.23	3.5	0.026
Whole milk	119	93	13	49	151	0.05	0.4	0.01
Low-fat milk	122	95	14	50	154	0.05	0.4	0.008
Skim milk	124	101	11	51	166	0.04	0.4	0.011
Yogurt whole milk	121	95	12	46	155	0.05	0.6	0.009
Acid whey powder	2054	1348	199	968	2288	1.24	6.3	0.05
Sweet whey powder	796	932	176	1079	2080	0.88	2.0	0.07

DNA, nucleosides, nucleotides, sugar phosphate) are in the aqueous phase. Pi is distributed between the aqueous and micellar phase and contributes to the mineral equilibrium of milk (Fig. 1). At pH 6.7, Pi is at 50% in the aqueous phase and 50% in the micellar phase to form nanoclusters of calcium phosphate previously described. During the transformation of milk in dairy products, Pi can be transferred to the aqueous phase, especially during acidification as previously described for Ca [13–17]. Consequently, it can be lost if the whey is removed, especially during cheese making. This explains the different levels of P determined in different dairy products (Table 2). Processed cheeses contain important amounts of P because melting salts corresponding to polyphosphates are added during the process.

From a nutritional point of view, the human needs of P are lower than Ca needs. There is no deficiency for this element, which is found in different foods and especially in cow milk and dairy products.

Magnesium (Mg)

In comparison to Ca, Mg is not abundant in milk and dairy products (Table 2). Its concentration in milk is about 120 mg/L (1200 mg/L for Ca). As described for Ca, 99% of this ion is located in skim milk. As Ca and Pi, it is distributed between micellar (50 mg/L) and aqueous (70 mg/L) phases. This ion is associated with Pi and citrate in the aqueous phase and in the nanoclusters of casein micelles. This distribution is sensitive to physicochemical conditions, especially acid pH. Thus, during milk acidification, this ion present in the micellar phase is solubilized in the aqueous phase of acidified milk [13–17]. In dairy products, the concentrations of Mg are variable depending on their manufacturing process (Table 2).

Despite their relatively low Mg concentration, dairy products can be considered sources of this ion (600 mL of milk provides 65 mg, corresponding to about 16% of the human recommended daily allowance).

Sodium (Na), Potassium (K), and Chloride (Cl)

These monovalent ions (cation for Na and K and anion for Cl) are mainly located in the aqueous phase of milk and dairy products, where they can be free or weakly associated with ions of opposite charge. It is noteworthy that in dairy products, the concentration of NaCl is increased by salting or brining (cheeses). In cheese technology, NaCl contributes to the draining of the curd, organoleptic properties of the cheeses, and selection of microorganisms and enzyme activities during ripening. The concentrations of NaCl depend on the cheese type (Table 2). Some cheeses contain important amounts of NaCl, such as Roquefort blue-veined cheese (Table 2). Other cheeses do not contain supplemented NaCl, such as lactic cheeses. Dietary intake of NaCl is considered to be too high since it may increase blood pressure. For this reason, different studies are in progress to reduce the quantity of NaCl in dairy products or to replace partially NaCl by KCl.

Iron (Fe)

Fe is not an abundant element in milk and dairy products made with cow milk [1] (Table 2). The concentration of Fe in milk is about 0.5 mg/L. It is noteworthy that the concentrations of Fe reported in the literature are sometimes variable. This variability is related to the different methods of sample preparation and analytical methods used for the determination. It can exist in 2 different states of ionization (Fe^{2+} or Fe^{3+}). In cow skim milk, iron is mainly associated with casein molecules, whey proteins, Pi, citrate [1,2,27], and lactoferrin. The concentration of lactoferrin is 0.1 and 1 g/L in cow and human milks, respectively.

Milk and dairy products are considered as very poor sources of Fe, and their contributions to the total Fe intake are very low. Thus, 600 mL of milk provides 0.3 mg (i.e., about 2.5% of the recommended daily allowance). In this context, different studies have been performed to enrich milk and dairy products with different forms of Fe [28–30]. In these iron supplementation studies, the technological, organoleptic, and nutritional aspects are evaluated.

Copper (Cu)

Like Fe, Cu is not abundant in milk and dairy products made with cow milk [2] (Table 2). The concentration of Cu in cow milk is about 0.1 mg/L; 2% are located in the lipid phase, 8% bound to whey proteins, 44% to casein, and 47% in a low-molecular-weight fraction (Pi and citrate ions) [2,27]. It is noteworthy that the concentrations of this element reported in the literature are sometimes variable. This variability is also related to the different methods of sample preparation and analytical methods used for the determination.

Overall, milk and dairy products are also considered poor sources of Cu, and their contribution to the copper intake is very low (600 mL of milk provides 0.3 mg, i.e., 5% of the recommended daily allowance).

Zinc (Zn)

Zn is a divalent cation present in milk at concentrations between 3 and 4 mg/L. In cow milk, most of the Zn is present in skim milk (99%), where it is mainly associated with casein micelles (95%) probably in interactions with Po and/or Pi of casein micelles. A small part is associated with citrate molecules in the aqueous phase [27,31,32].

Milk and dairy products (Table 2) contribute significantly to the zinc supply (600 mL of milk provides 2.4 mg corresponding to about 20% of the recommended daily allowance) [1,2].

Selenium (Se)

Se is present in different foods, especially in milk and dairy products [2,33–35]. It is a metalloid with similar properties to sulphur, often described as associated with glutathione peroxydase with an antioxidant role. Its concentration in milk is 30 μg/L. Se is not found in milk fat but mainly in skim milk, where it is associated with casein molecules and whey proteins [36]. The concentrations of this element in other dairy products are not well known. Milk is an important source of Se (600 mL of milk provides 20 μg of Se). Depending on the country, the contribution of dairy products to daily intake of Se is evaluated between 8% and 39% of the human recommended daily allowance [2].

VITAMINS OF MILK AND DAIRY PRODUCTS

Vitamins are organic substances classified into 2 categories depending on their chemical structures and physicochemical properties, especially solubility. The vitamins containing hydrophobic groups in their structure are named lipophilic vitamins (A, D, E, and K). Because of their hydrophobic structures, they are mainly located in the triglyceride milk fat. Consequently, these vitamins are found in whole milk, cream, butter, and cheeses. In the opposite, the hydrophilic vitamins (B_1, B_2, B_3, B_5, B_6, B_8, B_9, B_{12}, and C) are mainly located in skim milk. Their concentrations depend on the considered vitamins and dairy products (Table 3). A relative variability in the concentration of each vitamin is observed for several reasons, such as diet, microbial synthesis in the gastrointestinal tract, endogenous synthesis by the animal tissues, and a relative sensitivity of some vitamins to physical factors such as temperature, light, and O_2. On the other hand, as these compounds are present at low concentrations, it is not so easy to evaluate their contents in complex samples such as milk and dairy products.

The description of vitamins in milk and dairy products has been reviewed in detail in several special scientific publications [4–6].

Vitamin A (Retinol, Retinal, and Retinoic Acid)

Vitamin A is synthesized by plants. This compound exists in different forms: retinol (the major form), retinal, and retinoic acid. The concentrations of vitamin A in milk and different

Table 3. Concentrations of Vitamins in Some Dairy Products [7]

	Vitamin B_1 (Thiamin) mg/100 g	Vitamin B_2 (Riboflavin) mg/100 g	Vitamin B_3 (Niacin) mg/100 g	Vitamin B_5 (Pantothenic acid) mg/100 g	Vitamin B_6 (Pyridoxal) mg/100 g
Blue (USA)	0.029	0.382	1.016	1.729	0.166
Brick	0.014	0.351	0.118	0.288	0.065
Brie	0.070	0.520	0.380	0.690	0.235
Camembert	0.028	0.488	0.630	1.364	0.227
Cheddar	0.027	0.375	0.080	0.413	0.074
Cheshire	0.046	0.293	0.080	0.413	0.074
Cottage	0.021	0.163	0.126	0.213	0.067
Cream	0.017	0.197	0.101	0.271	0.047
Edam	0.037	0.389	0.082	0.281	0.076
Feta	0.154	0.844	0.991	0.967	0.424
Gouda	0.030	0.334	0.063	0.340	0.080
Gruyere	0.060	0.279	0.106	0.562	0.081
Limburger	0.080	0.503	0.158	1.177	0.086
Mozzarella (whole milk)	0.015	0.243	0.084	0.064	0.056
Munster	0.013	0.320	0.103	0.190	0.056
Neufchatel	0.015	0.195	0.126	0.566	0.041
Parmesan (grated)	0.045	0.386	0.315	0.527	0.105
Pasteurized Process Cheese	0.014	0.400	0.104	0.500	0.035
Port Salut	0.014	0.240	0.060	0.210	0.053
Provolone	0.019	0.321	0.156	0.476	0.073
Ricotta (whole milk)	0.013	0.195	0.104	0.213	0.043
Roquefort	0.040	0.586	0.734	1.731	0.124
Tilsit	0.061	0.359	0.205	0.346	0.065
Whole milk	0.038	0.162	0.084	0.314	0.042
Low fat milk	0.039	0.165	0.086	0.320	0.043
Skim milk	0.036	0.140	0.088	0.329	0.040
Yoghurt whole milk	0.029	0.142	0.075	0.389	0.032
Acid whey powder	0.622	2.060	1.160	5.632	0.620
Sweet whey powder	0.519	2.208	1.258	5.620	0.584

dairy products are reported in Table 3. Öste et al. [5] reported a mean concentration of 40 μg of vitamin A for 100 g of milk with a range between 10 and 100 μg. The content depends on several factors, especially animal feed, season, and fat content of milk. Vitamin A and derivates are reactive molecules sensitive to oxidation induced by O_2, light, or different oxidant agents. Thus, the concentrations of these compounds are partially reduced after heat treatments and acidification. The storage duration of products is also a factor inducing degradation of this vitamin. As described by Graulet in his review [4], the relative participation of milk and dairy products in the daily contribution varies according to nutritional habits, especially with regard to liver consumption by humans. The recommended daily allowance is estimated at 600–900 μg/d, and milk contributes 15%–20% of it.

Vitamin D (Ergocalciferol and Cholecalciferol)

Vitamin D refers to ergocalciferol (vitamin D_2) and cholecalciferol (vitamin D_3) synthesized by plants and by animal skin under sunlight influence, respectively. In bovine milk, the concentration of vitamin D is about 60 ng/100 g of milk, with a range between 10 and 120 ng/100 g [5]. Graulet [4] indicated vitamin activity between 27 and 47 IU/L of cow milk. Vitamin D is considered relatively instable. Losses can be observed after exposure to light, O_2, heat, and acidic conditions. As the recommended daily allowance is estimated between 200 and 1000 UI per day, the contribution of dairy products to vitamin D supply is low. Milk and dairy products cannot be considered as interesting sources of this vitamin. For this reason, different liquid milks are sometimes enriched with vitamin D to improve the use of Ca by organisms and to prevent vitamin D–related diseases such as osteoporosis. The vitamin D concentration of enriched milk is about 0.3–0.4 μg/100 g of milk [5].

Vitamin E (Tocopherols and Tocotrienols)

Vitamin E refers to 8 different natural forms synthesized by plants and belonging to 2 major categories: tocopherols and tocotrienols. The major compound found in milk is α-tocopherol. The concentrations of vitamin E in milk and different dairy products are reported in Table 3. This vitamin is mainly found in cream and butter because of its hydrophobicity. The vitamin E content of milk is low, with a value of 100 μg/100 g (range, 20–180 μg/100 g) [5]. Graulet [4] indicated a

Table 3. Extended.

Vitamin B_9 (Folic acid) μg/100 g	Vitamin B_{12} (Cobalamine) μg/100 g	Vitamin A (Retinol) IU	Vitamin A (Retinol) RE	Vitamin E (Tocopherol) ATE	Vitamin C (Ascorbate) mg/100 g
36.4	1.217	721	228	0.640	0
20.3	1.257	1083	302	0.500	0
65.0	1.650	667	182	0.655	0
62.2	1.296	923	252	0.655	0
18.2	0.827	1059	303	0.360	0
18.2	0.827	985	245	ND	0
12.2	0.623	163	48	0.122	0
13.2	0.424	1427	437	0.941	0
16.2	1.535	916	253	0.751	0
32.0	1.690	447	128	0.030	0
20.9	1.535	644	174	0.350	0
10.4	1.600	1219	301	0.350	0
57.5	1.040	1281	316	0.640	0
7.0	0.654	792	241	0.350	0
12.1	1.473	1120	316	0.465	0
11.3	0.264	1134	264	ND	0
8.0	1.400	701	173	0.800	0
5.8	2.300	856	243	ND	0
18.2	1.500	1333	372	0.500	0
10.4	1.463	815	264	0.350	0
12.2	0.338	490	134	0.350	0
49.0	0.643	1047	299	ND	0
20.0	2.100	1045	291	0.701	0
5.0	0.357	126	31	0.100	0.940
5.1	0.364	205	57	0.070	0.950
5.2	0.378	204	61	0.040	0.980
7.4	0.372	123	30	0.088	0.530
33.2	2.500	58	9	0.015	0.900
11.6	2.371	44	10	0.029	1.490

concentration of vitamin E between 0.2 and 1 mg/L of bovine milk. Because of its chemical structure containing several double bonds, vitamin E is sensitive to oxidation induced by O_2, photo-oxidation, trace elements such as Fe^{3+} and Cu^{2+}, or different oxidant agents. Heat treatment and acidification induce a decrease of the active forms [4–6]. However, if the conditions are not oxidative, this vitamin is stable at a temperature up to 100°C [5]. The recommended daily allowance is estimated at 15 mg per day, and consequently, the contribution of milk to vitamin E supply is low.

Vitamin K (Vitamins K1 or Phylloquinone and Vitamins K2 or Menaquinone)

Both of these groups (K1 and K2) of vitamins K are synthesized by plants and bacteria from rumen, respectively. The concentration of this vitamin K is very low in milk (between 0.4 and 1.8 μg/100 g), but fermented products, especially cheeses, have been reported to contain significant quantities of menaquinones (40–80 μg/100 g) [4].

The recommended daily allowances are 90 and 120 μg/d for women and men, respectively. Thus, milk and dairy products are not important contributors to vitamin K intake.

Vitamin B_1 (Thiamine)

Vitamin B_1 is synthesized by plants, yeast, and bacteria. It is soluble in water and insoluble in the lipid phase of milk. In skim milk, this vitamin is free, phosphorylated, or associated with protein. The concentrations of this vitamin in milk and different dairy products are reported in Table 3. Graulet [4] indicated a concentration of 0.44 mg/L in whole cow milk. Öste et al. [5] reported concentrations between 20 and 80 μg/100 mL. Breed, feed, and season have little influence on the thiamine content of cow milk. On the other hand, this vitamin is considered as stable during pasteurization, but it is partially degraded after UHT treatment (20%–40%). Ultraviolet irradiation induces inactivation of this vitamin. The recommended daily allowance is about 1.2 mg per day. Milk can be considered a source of this vitamin for humans because it contributes between 10% and 20% to the recommended daily allowance. More precisely, 250 mL of milk provides 12% of the recommended daily allowance.

Vitamin B_2 (Riboflavin)

Vitamin B_2 is synthesized by plants and microorganisms, especially bacteria present in rumen. The concentrations of vitamin B_2 in milk and different dairy products are reported in Table 3. Graulet [4] indicated a concentration of 1.83 mg/L in whole cow milk, while Öste et al. [5] indicated a similar average content in milk of 170 μg/100 g (range between 80 and 250 μg/100 g). The content varies with breed and season. This vitamin is stable to heat treatment and acid conditions. In the opposite, riboflavin is unstable at alkaline pH and can be degraded by light. To avoid the degradation, it is necessary to use adapted packaging materials. The recommended daily allowance is 1.3 mg per day, and milk contributes between 60% and 80% to these recommended daily allowances. More precisely, 250 mL of milk corresponds to 27% of RDA for vitamin B_2. Thus, milk and dairy products are considered as important contributors of this vitamin.

Vitamin B_3 (Niacin and Nicotinamide)

This vitamin refers to niacin (or nicotinic acid) and nicotinamide, which are 2 precursors of nicotinamide adenine dinucletotide (NAD^+) and nicotinamide dinucleotide phosphate ($NADP^+$). The concentrations of vitamin B_3 in milk and different dairy products are reported in Table 3. Graulet [4] indicated a concentration of 1.07 mg/L in whole cow milk. For Öste et al. [5], the mean content of niacin in cow milk is about 94 μg/100 g, with a range from 30 to 200 μg/100 g. This vitamin is considered one of the most stable vitamins. Indeed, the chemical structure of niacin is insensitive to heat, air, and light. The recommended daily allowance is 12–16 mg per day, and milk contributes between 1% and 4% to it.

Vitamin B_5 (Pantothenic Acid)

Vitamin B_5 is pantothenic acid. Its concentration in milk and different dairy products is reported in Table 3. Graulet [4] indicated a concentration of 3.62 mg/L in cow milk. For Öste et al. [5], the mean content in cow milk is about 0.35 mg/100 g, with a range from 0.26 to 0.49 mg/100 g. The content of this vitamin depends on the breed, feed, and season. This compound is stable at neutral pH, but it can be modified at alkaline and acid pH. Yogurts contain less vitamin B_5 (0.15 to 0.44 mg/100 g). The recommended daily allowance for humans is 5 mg/d.

Vitamin B_6 (Pyridoxal)

Vitamin $B_{6,}$ synthesized by plants and microorganisms, refers to 3 different compounds: pyridoxal (the major form in milk), pyridoxine, and pyridoxamine. These molecules lead, after biochemical modifications, to the pyridoxal-5′-phosphate, a cofactor implicated in different reactions. The concentrations of this vitamin in milk and different dairy products are reported in Table 3. Graulet [4] indicated a concentration of 0.36 mg/L and Öste et al. [5] a mean content of about 64 μg/100 g, with a range between 22 and 190 μg/100 g. In milk, about 14% of vitamin B_6 is found in the bound form and 86% in the free form. These concentrations vary according the stage of lactation, diet, and season. Heat treatment and time of storage after this treatment and ultraviolet light negatively affect the content in this vitamin. The recommended daily allowance is 1.3–1.7 mg/d, and milk and dairy products are not good sources of this vitamin. Milk contributes 5% to 20% to the recommended daily allowance.

Vitamin B_8 (Biotin)

Vitamin B_8 is synthesized by plants and rumen microorganisms. The milk concentration of vitamin B_8 is strongly related to the cow's dietary intake. The concentration of this vitamin is 8 μg/L of milk [4]. For Öste et al. [5], the mean content of biotin in cow milk is about 3.1 μg/100 g, with a range between 1.2 and 6.0 μg/100 g. Losses of biotin due to different physicochemical conditions used in the dairy industry are small. The recommended daily allowance is between 20 and 30 μg/d, and consequently milk contributes significantly to vitamin B_8 supply.

Vitamin B_9 (Folate)

As with some vitamins previously described, vitamin B_9 is synthesized by plants and microorganisms. In milk, this vitamin can be free or bound to folate-binding proteins. The concentrations of vitamin B_9 in milk and different dairy products are reported in Table 3. Graulet [4] indicated a concentration of this vitamin between 50 and 90 μg/L of cow milk. Öste et al. [5] reported a folate content of about 5 μg/100 g, with a range between 3.7 and 7.2 μg/100 g. Seasonal variations are described, with higher concentrations found in summer compared with winter. It is noteworthy that bacteria used to manufacture different dairy products can synthesize this vitamin *in situ*. This explains the concentrations between 8 and 10 μg/100 g of this vitamin in buttermilks and yogurts. This vitamin is very sensitive to different physicochemical conditions used in the dairy industry, especially UHT treatment (but not pasteurization) and presence of O_2. The recommended daily allowance is about 400 μg/d, and milk contributes 3% to 10% to human intake.

Vitamin B_{12} (Cobalamines)

This vitamin originates exclusively from microbial synthesis in the rumen. It is a cyclic molecule containing in its central structure a cobalt ion. In milk, this vitamin is mainly bound to protein. The concentrations of vitamin B_{12} in milk and different dairy products are reported in Table 3. Graulet [4] indicated a concentration of 4.4 μg of vitamin B_{12}/L of cow milk. For Öste et al. [5], the concentration is about 0.4 μg/100 g of cow milk, with a range between 0.24 and 0.74 μg/100 g. The content is very dependent on the intake of cobalt by the cow. The concentrations of this vitamin can also be reduced by exposure to radiation, UHT treatment, and time of storage after this type of treatment. In fermented milk, this vitamin is metabolized by microorganisms used for the fermentation. The recommended daily allowance is 2.4 μg/d, and milk contributes largely to human intake. More precisely, 250 mL of milk provides 24% of the recommended daily allowance.

Vitamin C (Ascorbic Acid)

Vitamin C is found in 2 states of oxidation corresponding to ascorbic and dehydroascorbic acids. Ascorbate is reversibly oxidized with the loss of one electron to form dehydroascorbic acid. Öste et al. [5] reported a mean content of vitamin C in cow milk of 2.11 mg/100 g, with a range between 1.65 and 2.75 mg/100 g. Concentration varies according to the seasons (winter > summer). As shown in Table 3, vitamin C is present in milk but not in dairy products. This decrease corresponds probably to a degradation of this vitamin during the processing of dairy products. It is reported that vitamin C is very sensitive to light and heat treatment, especially UHT treatment. These sensitivities are strongly dependent on the O_2. The recommended daily allowance is 75 and 90 mg/d for women and men, respectively. Milk and dairy products can be considered as poor sources of vitamin C. They provide between 2% and 15% of the recommended daily allowance.

CONCLUSION AND PERSPECTIVES

Milk and dairy products constitute real and unique sources of micronutrients, which have generated extensive investigations for more than 60 years. As a result of these studies, it appears that these micronutrients are various in terms of concentration, form, location, and interaction with the other compounds present in milk and dairy products. Knowledge of minerals is relatively complete and precise. As far as vitamins are concerned, the data are lacking, or there is discrepancy between them (some vitamins are easily modified by external factors, difficulty to be quantified due to sample preparation, and the use of appropriate analytical methods).

However, there is no doubt about their important nutritional role and health benefits. Despite this knowledge, several questions still arise:

- What is the content of each vitamin in different dairy products?
- What are the changes that may occur in the micronutrients while the dairy products are being processed?
- What are the effects of compounds present in other foods on the absorption of these micronutrients?
- Is it nutritionally interesting to enrich dairy products with micronutrients?

All of these questions are being studied in research projects that are in progress and for the future.

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REFERENCES

1. Flynn A: Minerals and trace elements in milk. Adv Food Nutr Res 36:209–252, 1992.
2. Flynn A, Cashman K: Nutritional aspects of minerals in bovine and human milk. In Fox PF (ed): “Advanced Dairy Chemistry: Lactose, Water, Salts and Vitamins,” vol 3, 2nd ed. London: Chapman & Hall, pp 257–302, 1997.
3. Fransson GB, Lonnerdal B: Distribution of trace elements and minerals in human and cow’s milk. Pediatr Res 17:912–915, 1983.
4. Graulet B: Improving the level of vitamins in milk. In Griffiths MW (ed): “Improving the Safety and Quality of Milk: Improving Quality in Milk Products,” vol. 2. Boca Raton, FL: CRC Press, pp 229–251, 2010.
5. Öste R, Jägerstad M, Anderson I: Vitamins in milk and milk products. In Fox PF (ed): “Advanced Dairy Chemistry: Lactose, Water, Salts and Vitamins,” vol 3, 2nd ed. London: Chapman & Hall, pp 347–402, 1997.
6. Schaafma G: Vitamins. In Roginski H, Fuquay JW, Fox PF (eds): “Encyclopedia of Dairy Sciences,” vol 4, 1st ed. New York: Academic Press, pp 2653–2657, 2003.
7. Kosikowski FV, Mistry VV: “Cheese and Fermented Milk Foods: Origins and Principles,” vol 1, 3rd ed. Westport, CT: F.V. Kosikowski, pp 684–697, 1997.
8. McGann TCA, Buchheim W, Kearney RD, Richardson T: Composition and ultrastructure of calcium phosphate–citrate complexes in bovine milk systems. Biochim Biophys Acta 760:415–420, 1983.
9. Holt C: Structure and stability of bovine casein micelles. Adv Protein Chem 43:63–151, 1993.
10. Holt C: The milk salts and their interaction with casein. In Fox PF (ed): “Advanced Dairy Chemistry: Lactose, Water, Salts and Vitamins,” vol 3, 2nd ed. London: Chapman & Hall, pp 233–254, 1997.
11. Holt C: An equilibrium thermodynamic model of the sequestration of calcium phosphate by casein micelles and its application to the calculation of the partition of salts in milk. Eur Biophys J 33:421–434, 2004.
12. Mekmene O, Le Graët Y, Gaucheron F: A model for predicting salt equilibria in milk and mineral-enriched milks. Food Chem 116:233–239, 2009.
13. Mekmene O, Le Graët Y, Gaucheron F: Theoretical model for calculating ionic equilibria in milk as a function of pH: comparison to experiment. J Agric Food Chem 58:4440–4447, 2010.
14. Gaucheron F: “Minéraux et Produits Laitiers.” Paris: Tec et Doc, 2004.

15. Gaucheron F, Le Graet Y, Schuck P: Equilibres minéraux et conditions physicochimiques. In Gaucheron F (ed): "Minéraux et Produits Laitiers." Paris: Tec et Doc, pp 219–280, 2004.
16. De la Fuente MA: Changes in the mineral balance of milk submitted to technological treatments. Trends Food Sci Tech 9:417–428, 1998.
17. Le Graët Y, Brulé G: Equilibres minéraux du lait: influence du pH et de la force ionique. Lait 73:51–60, 1993.
18. Bottazzi V, Battistotti B, Bianchi F: The microscopic crystalline inclusions in Grana cheese and their X-ray microanalysis. Milchwissenchaft 37:577–580, 1982.
19. Brooker BE, Hobbs DG, Turvey A: Observations on the microscopic crystalline inclusions in cheddar cheese. J Dairy Res 42:341–348, 1975.
20. Brooker BE: The crystallisation of calcium phosphate at the surface of mould-ripened cheeses. Food Microstruct 6:25–33, 1987.
21. Karahadian C, Lindsay RC: Integrated roles of lactate, ammonia, and calcium in texture development in mold surface-ripened cheese. J Dairy Sci 70:909–918, 1987.
22. Metche M, Fanni J: Rôle de la flore fongique dans l'accumulation du calcium et du phosphore à la surface des fromages type Camembert. Lait 58:337–354, 1978.
23. Morris HA, Holt C, Brooker BE, Banks JM, Manson W: Inorganic constituents of cheese: analysis of juice from a one-month-old Cheddar cheese and the use of light and electron microscopy to characterize the crystalline phases. J Dairy Res 55:255–268, 1988.
24. Pointillart A, Guéguen L: Intérêts nutritionnels du calcium et du phosphore des produits laitiers. In Gaucheron F (ed): "Minéraux et Produits Laitiers." Paris: Tec et Doc, pp 703–738, 2004.
25. Philippe M, Gaucheron F, Le Graët Y, Garem A, Michel F: Physicochemical characterization of calcium-supplemented skim milk. Lait 83:1–15, 2003.
26. Philippe M, Gaucheron F, Le Graët Y: Physicochemical characteristics of calcium supplemented skim milk: comparison of three soluble calcium salts. Milchwissenchaft 59:498–504, 2004.
27. Brulé G, Fauquant J: Interactions des protéines du lait et des oligoéléments. Lait 62:323–331, 1982
28. Gaucheron F, Le Graët Y, Raulot K, Piot M: Physico-chemical characterization of iron-supplemented skim milk. Int Dairy J 7:141–148, 1997.
29. Gaucheron F: Iron fortification in dairy industry. Trends Food Sci Tech 11:403–409, 2000.
30. Hekmat S, McMahon DJ: Distribution of iron between caseins and whey proteins in acidified milk. Lebensm Wiss u Technol 31:636–638, 1998.
31. Blakeborough P, Salter DN, Gurr MI: Zinc binding in cow's and human milk. Biochem J 209:505–512, 1983.
32. Singh H, Flynn A, Fox PF: Binding of zinc to bovine and human milk proteins. J Dairy Res 56:235–248, 1989.
33. Navarro-Alarcon M, Cabrera-Vique C: Selenium in food and the human body: a review. Sci Total Environ 400:115–141, 2008.
34. Sanz Alaejos M, Diaz Romero C: Selenium concentration in milks. Food Chem 52:1–18, 1995.
35. Foster LH, Chaplin MF, Sumar S: The effect of heat treatment on intrinsic and fortified selenium levels in cow's milk. Food Chem 62:21–25, 1998.
36. Van Dael P, Vlaemynck G, Van Renterghem, Deelstra H: Selenium content of cow's milk and its distribution in protein fraction. Z Lebensm Unters Forsch 192:422–426, 1991.

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