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Original Article

Analysis of Minor and Trace Elements in Cow, Goat and Sheep Milk in the NW Part of Romania

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Abstract

A number of 40 cow, goat and sheep milk samples were collected in NW part of Romania and analyzed to determine 15 minor and trace elements (As, Be, Bi, Cd, Co, Cr, Cs, Cu, Mn, Ni, Pb, Rb, Se, Sr and Zn) in fresh cow, goat and sheep milk by inductively coupled plasma-mass spectrometry, ICP-MS. The levels of minor and trace elements are an important indicator of safety and quality of milk. While some elements are essential at low levels, an excess can cause deleterious health effect in humans. The elements were categorized into minor elements (concentration more than 100 ng/g and decreasing order: Zn>Rb>Sr>Cu>Mn>Se>Cr>Ni), trace elements (concentration below 10 ng/g and decreasing order: Cs>Be>Co>Bi) and potential toxic trace elements (As, Cd and Pb). The levels of toxic trace elements, including As, Cd and Pb were low.

Keywords: minor elements, trace elements, milk, NW Romania.

1. Introduction

Milk and dairy products are important for human diet and in particular provide minerals and proteins, which are essential for the growth and maintenance of human and animals. In spite of being a good product regarding its nutrition value, sheep milk cannot be compared by its production volume with either cow or goat milk.

All milk contains the same kind of constituents but in varying amount. In general, the gross composition of cow's milk in U.S. is 87.5% water, 4.9% lactose (carbohydrate), 3.4% fat, 3.3% protein, and 0.7% minerals (referred to ash) [5] .

Many trace elements (Fe, Mn, Cu, Zn, etc) are essential for biological processes and hence play an important role in the normal growth and development of all human beings in general and children in particular.

During early infancy, the requirement of trace elements is more critical; because of higher growth rate than during any other period of life. Consequently, the deficiency of minor and trace elements can lead to various disorders. Cow milk is considered an ideal food for infants, while the goat milk possesses special attributes such as high digestibility, distinct alkalinity, high buffering capacity and certain therapeutic values in medicine [7]. The level of trace and minor elements in milk and dairy products depends on the species, genetic factors (breed), season, nutritional status of the animal, stage of lactation, environmental conditions and storage.

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Furthermore, technological treatments, geographical localization and the quality of feed material are very important for the level of minor and trace elements in dairy products.

Despite the essential benefits of milk consumption, the contamination of milk from agricultural practices, environmental pollution, animal feeds and the use of sewage sludge in agriculture require special [4].

The presence of heavy metals in milk is controlled in accordance with the defined maximum levels set by EU [1].

The concentrations of selected minor and trace elements such as As, Be, Bi, Cd, Co, Cr, Cs, Cu, Mn, Ni, Pb, Rb, Se, Sr and Zn in fresh cow, goat and sheep milk were determined using inductively coupled plasma mass spectrometry (ICP-MS). In general, the mean concentrations in sheep were found to be higher than those of the cow and goat milk.

2. Material and Method

Reagents and standards

The calibration standard solutions were prepared from ICP-MS Multi-Element Calibration Standard 3 Perkin-Elmer, 10 mg/l. All reagents (HNO_3 65%, H_2O_2 30%) used for this research work were of analytical grade and were purchased from Merck, Darmstadt, Germany. The certified reference material (NIST-SRM 1549 Whole milk powder) was obtained from LGC Promochem GmbH, Wessel, Germany. All glassware were cleaned with nitric acid prior to use. For all dilutions, ultrapure water (18.2 MΩ/cm) obtained from a Millipore Direct-Q3 UV system (Millipore, France) was used. Plastic and glassware were cleaned by soaking in diluted HNO3 (1:9, v/v), rinsing with ultrapure water and drying prior to use.

Sampling and sample preparation

For the present study, the fresh milk samples were collected from rural area from NW part of Romania, Cluj County, during May-July 2014: 19 cow milk, 6 goat milk and 15 sheep milk.

The udder of each cow was washed before milking and approximatively 200 ml milk samples were collected directly in acid-washed polyethylene bottles.

Upon collection, all milk samples were homogenized, labeled and stored at -20°C until analysis.

1 ml of samples were acid digested in 8 ml HNO_3 65% and 2 ml H_2O_2 30% in a microwave closed system at 200°C, 1000W, for 20 min. [10]. After cooling down to room temperature, the samples were quantitatively transferred to 25 mL volumetric flasks and diluted to the mark with double deionized water.

All digestions were made in triplicate. Certified reference material NIST 1549 and blank, consisting of deionized water and reagents, were prepared in the same way as the sample. All determinations were carried out in triplicate.

Instruments

For the microwave digestion of samples, a closed-vessel microwave system Berghof MWS-3+ with temperature control mode (Eningen, Germany) was used. The contents of minor and trace elements (As, Be, Bi, Cd, Co, Cr, Cs, Cu, Mn, Ni, Pb, Rb, Se, Sr and Zn) were determined by inductively coupled plasma mass spectrometer, ICP-MS (ELAN DRC II, SCIEX, Perkin Elmer, Toronto, Canada).

3. Results and discussions

The obtained concentrations (mean ± SD) of analysed 15 elements in cow, goat and sheep milk are presented in Table 1.

The elements were categorized into minor elements (concentration more than 100 ng/g and decreasing order: Zn>Rb>Sr>Cu>Mn>Se>Cr>Ni), trace elements (concentration below 10 ng/g and decreasing order: Cs>Be>Co>Bi) and potential toxic trace elements (As, Cd and Pb).

Co, Cu, Zn, Mn, Se and Zn are essential elements for human and animals, since they are involved in a variety of physiological processes.

These elements are required components of proteins, enzymes and redox systems, therefore, deficiency or excessive intake in humans can lead to several disorders and diseases [6].

In order to check the accuracy of the method, CRM (NIST-1549 non-fat milk powder) was analyzed for the determination of Cd, Pb, Cr, Cu, Se, Mn, Zn, As and Co. The recovery value means of all the investigated elements were found to be within the interval of confidence ($p < 0.05$), calculated for the value certified.

The limits of detection (LOD) and limits of quantification (LOQ), were calculated with three and ten times the standard deviation of the blank divided by the slope of the analytical curve, respectively [13].

The limits of quantification (LOQ, µg/l) in milk were found to be: As (1.0), Be (3.4), Bi (2.9), Cd (0.4), Co (0.8), Cr (2.0), Cs (3.2), Cu (0.5), Mn (6.5), Ni (0.1), Pb (4.0), Rb (4.2), Se (2.2), Sr (4.5) and Zn (6.9).

Table 1 Mean concentrations of investigated elements (µg/l) with standard deviation in cow, goat and sheep milk.

	Cow milk (n=19)	**Goat milk (n=6)**	**Sheep milk (n=15)**
Minor elements			
Cr	18.2 ± 1.32	11.1 ± 1.45	25.6 ± 2.33
Cu	75.6 ± 11.1	58.6 ± 7.83	98.9 ±10.1
Mn	32.7 ± 5.63	25.6 ± 7.84	89.3 ± 11.2
Ni	3.61 ± 0.89	5.80 ± 2.45	4.32 ± 2.01
Rb	1985 ± 456	1978 ± 521	1945 ± 457
Sr	423 ± 89.5	412 ± 78.9	456 ± 56.4
Zn	2356 ±231	3046 ±112	2254 ± 110
Se	21.2 ± 2.35	20.4 ±1.84	24.5± 2.34
Trace elements			
Be	2.23 ± 1.23	1.96 ± 1.04	3.23 ± 1.25
Bi	1.92 ± 1.45	1.23 ± 1.12	1.94 ± 0.45
Co	1.56 ± 0.53	1.23 ± 0.47	2.21 ± 0.89
Cs	5.23 ± 3.12	4.56 ± 2.23	6.01 ± 1.78
Toxic trace elements			
As	<LOQ	<LOQ	<LOQ
Cd	2.56 ± 1.53	3.56 ± 2.01	5.25 ± 1.85
Pb	15.8 ± 5.45	20.5 ± 6.12	35.6 ± 6.82

Minor elements. The average concentrations of Ni, Rb, Sr and Se were similar in all types of milk (cow, goat and sheep); but Cr, Cu and Mn in cow and sheep milk were higher than in goat milk. On the contrary, Zn concentrations in goat milk were significantly higher in the goat milk (3046 µg/l) compared to cow (2356 µg/l) and sheep (2254 µg/l), respectively. The comparison of results obtained in this study to published literature revealed that that all minor elements were lower than data reported by Khan et al., 2014 [14].

The content of Cr, Cu and Se was higher, while Ni was lower than Crespo et al., 2013 [10]. The content of Zn was the same as reported in milk of Simmental and Holstein-Friesian cows from Poland [9]. The levels of investigated essential elements were appropriate and thus milk can make a contribution of these elements to the daily recommended intake for all age groups [3; 15.]

Trace elements. From the literature, the obtained concentrations of Co were found lower than cow's milk, NW Spain [10] and South Korea [14]. Concentrations of analyzed minor elements in analyzed samples were proportionally increased with the corresponding specific gravity (density) of milk samples (cow milk: 1.032-1.040 g/ml, goat milk: 1.029-1.039 g/ml and sheep milk: 1.035-1.038 g/ml, respectively) [8].

Toxic trace elements. Arsenic was not detectable in any of the samples.

No maximum statutory limits have been established for arsenic and cadmium in milk and lead concentrations were below the statutory limit established by the EU (20 µg/kg wet weight) [1]. The lead and cadmium concentrations in sheep milk were significantly higher than those in cow and goat milk, respectively.

This results, confirm the hypothesis that cadmium and lead are mainly associated with the protein fraction (casein fraction) [2].

Park et al., 2007 [8] have reported that the protein content in sheep milk (5.8% wet weight) is higher than goat (4.6% wet weight) and cow milk (3.3% wet weight). Moreover, the results of this work indicate that Cd and Pb concentrations in milk tend to increase by age.

The mean concentrations of Cd and Pb in all milk samples from animals aged ≥ 5 years were higher [Cd - 2.86 µg/l (cow), 4.10 µg/l (goat) and 5.61 µg/l (sheep), Pb – 17.9 µg/l (cow), 23.2 µg/l (goat) and 39.1 µg/l (sheep)], compared to cows aged < 5 years [Cd – 2.25 µg/l (cow), 2.86 µg/l (goat) and 2.56 µg/l (sheep), Pb – 13.7 µg/l (cow), 17.6 µg/l (goat) and 32.1 µg/l (sheep)]. These results were similar with those reported by Rubio et al., 1998 [12]

4. Conclusions

The results of this study provide valuable data regarding minor and trace elements in cow, goat and sheep milk samples.

Results presented in this work also suggest significantly lower concentration of Cr, Cu, Mn and Zn in goat milk than in cow and sheep milk. Concentrations of analyzed trace elements in analyzed milk samples were proportionally increased with the corresponding density of milk samples (goat < cow < sheep).

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