Copper Concentrations Of Cow's And Sheep's Milk Collected In Harran Lowland Of Turkey

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Abstract: The presence of essential elements in milk is vital for the nutrition of human beings and also all mammalians, particularly infants. The aim of this study was to determine the concentrations of copper in cow's and sheep's milk by inductively coupled plasma-mass spectrometer (ICP-MS) after microwave-assisted digestion with nitric acid and hydrogen peroxide. Between February 2017 to July 2017, 21 cow's milk samples and 40 sheep's milk samples were gathered from two different regions of Harran lowland. The mean concentration of copper in cow's milk samples were 97.21 ± 6.33 ppb and in sheep's milk samples were 135.13 ± 31.05 ppb, respectively. It was seen that there was a statistical difference between the levels of copper in cow's and sheep's milk. The data revealed that copper levels in sheep's milk were higher than the cow's milk. ICP-MS method of this study could provide a sensible alternative for the element characterization of milk samples.

Index Terms: Cow's milk, Sheep's milk, Copper, ICP-MS.

1 Introduction

Milk; is a biological fluid and food with vital importance for humans, mammals and especially newborns. Milk and dairy products are important sources for meeting the daily requirement of essential elements [1]. Milk nearly contains all of the essential nutrients as well as all the essential elements that will provide newborn growth [2]. However, the quantities of essential elements in the milk vary according to the race of the animal, the dietary pattern, the lactation period, and the geographical region in which it is grown [3]. Essentially accepted elements of human and mammalian nutrition can be classified as macro and trace elements. Macro elements such as iron, zinc, manganese, selenium, iodine, chromium, cobalt, molybdenum and copper, while sodium, potassium, chlorine, calcium, magnesium, and phosphorus are the trace elements. All these elements are present in varying amounts in the milk [4]. These elements are found in different chemical forms depending on organic molecules such as inorganic ions and salts, proteins, oils or carbohydrates in milk [1]. Copper is an essential element that plays a critical role in oxidation-reduction reactions in mammalian metabolism [5]. Copper is also essential for the hemoglobin synthesis, absorption of iron, and glucose metabolism [6]. Copper may be found at high levels in sheep, although it is common for copper deficiency in ruminants [7]. Several studies have reported the occurrence of the copper element of cow's milk in all over the world [8], [9], [10], [11]. The content of copper in sheep's milk was widely reported in all over the world [5], [12], [13], [14].

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The aims of this study were 1. to determine the content of copper in cow's and sheep's milk in originating from Turkey, 2. to report the first comparison of copper levels between two types of animal milk, 3. to discuss to result with reported data in worldwide.

2 Materials and Methods

2.1 Sample Collection

A number of 21 cow and 40 sheep raw milk samples (200 ml) were collected into sterile polyethylene tubes between February to July 2017 from small family farms throughout Harran Lowland of Turkey. The cows and sheep were housed in loose barn system with adlibitum fodder and water. Milking of animals was performed twice a day at and interval of 10 hours. After collection, milk samples were transported to the laboratory in a cooler and were stored at -20^{o}C until analyses.

2.2 Copper analyses

Raw milk samples were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) (Agilent 7500 ce, Japan) with radiofrequency power: 1500 W, Plasma gas flow rate (L min^{-1}): 15, Auxiliary gas flow rate (L min^{-1}): 1, Carrier gas flow rate (L min^{-1}): 1.1, dwell time: 50 ms, plasma gas: Ar, operational parameters. The isotope $^{63}Cu^{+}$ was detected.

2.3 Statistical analyses

The copper composition of raw milk samples was performed using SPSS 11.0 software package. Concentrations were tested as a minimum, mean ± standard deviation, and maximum levels. One-way analyses of variance were performed for differences in copper concentrations of milk samples and considered as significant at $P < 0.05$.

3 Results and Discussion

As the suitability of cow and sheep milk for the dairy industry, especially in cheese and yogurt production, depends on its elemental composition. Table 1. reports the minimum, mean, standard deviation, and maximum levels of cow's, sheep's and overall raw milk samples in ppb weight bases. Raw milk samples from two different species showed very different copper composition. This can probably be interpreted by the fact that feeding behavior, biological and genetic differences.

Table 1: *Copper concentration of cow's and sheep's milk samples*

Cu (ppb)	Sample no	Minimum	Mean±SD	Maximum
Cow's milk	21	54.0	97.21 ± 6.33	160.0
Sheep's milk	40	9.8	135.13 ± 31.05	727.0

In this study, the average of the concentrations of copper in cow's milk was higher than the cow's milk samples from regional farms in Croatia with a mean concentration of 13±11 ppb in a range of 10-64 ppb [11]. Copper concentration in cow's milk samples were reported by various studies is highly variable, 1730 ppb mean copper concentration was reported by Soares et al. [15] and 380 ppb copper concentration was reported by Sikiric´ et al. [16] whereas some other authors have reported 12-737 ppb of copper concentration in cow's milk [17]. As compared to the copper concentration in milk of Poland cows (64.3 ppb) this study showed higher copper concentrations [18]. The average copper concentration of cow milk samples from Spain (60 ppb) was lesser than this study results [19]. Copper concentrations of cow milk samples of a study ranged from 0.41-0.46 ppb which is lower than our mean concentration [20]. Noe¨l at al., [21] have also reported parallel copper content in cow's milk with this study (Table 2).

Table 2: *Copper concentration of cow's milk from different regions.*

Author	Region	No of sample	Mean Cu concentration (ppb)	Method	Year
Zhou et al.	China	20	32.02	ICP-MS	2016
Elbagermi et al.	Libya	-	170	MP-AES	2014
Bilandzic et al.	Croatia	45	13.0	ICP-OES	2012
Soares et al.	Brasil	54	1730	FAAS	2004
Sikiric´ et al.	Croatia	60	380	FA-AAS	2003
Dobrzanski et al.	Poland	24	65-89	ICP-MS	2005
Noe¨l et al.	France	38	91.0	ICP-MS	2012
Martino et al.	Spain	1	60.0	DF-ICP-MS	2001
Licata et al.	Italy	40	12-737	GFAAS	2004
This study	Turkey	21	97.21	ICP-MS	2017

Abbreviations: ICP-MS, Inductively Coupled Plasma - Mass Spectrometry; FAAS, Flame Atomic Absorption Spectrometry; ICP-OES, Inductively Coupled Plasma – Optical Emission Spectrometry; MP-AES, Microwave plasma- Atomic Emission Spectrometry; FA-AAS, Flame Aspiration- Atomic Absorption Spectrophotometry, DF-ICP-MS, Double Focusing- Inductively Coupled Plasma - Mass Spectrometry; GFAAS, Graphite Furnace Atomic Absorption Spectrometry. Ruminants normally fall in with copper deficiencies, especially sheep have suboptimal levels of copper [7]. The copper content in sheep's milk was significantly higher than the content of cow's milk. Average copper concentrations of sheep's milk samples were lesser than the reference concentration of 243 ppb and 304 ppb [22]. Copper content in sheep's milk was also lesser than reported by Licata et al. [23], and Elbagermi et al. [8]. Miedico et al. [13] have reported 130 ppb copper content in the milk of Italian sheep which is similar to this study results. Whereas, 60 ppb copper content in the milk of Croatian sheep has been reported by Antunović et al. [24]. Differences in copper content of cow and sheep milk may be originated to feed, lactation period or the genus of the animals (Table 3).

Table 3: *Copper concentration in sheep's milk from different regions*

Author	Region	Number of samples	Mean Co concentration (ppb)	Method	Year
Miedico et al.	Italy	46	130	Q-ICP-MS	2012-2013
Khan et al.	Pakistan	20	243-304	FAAS	2006
Licata et al.	Italy	10	340	ICP-AES	2012
Antunović et al.	Croatia	23	60	ICP-OES	2016
Elbagermi et al.	Libya	-	201	MP-AES	2014
This study	Turkey	40	135.13	ICP-MS	2017

Abbreviations*:* Q-ICP-MS, Quadrupole- Inductively Coupled Plasma - Mass Spectrometry; FAAS, Flame Atomic Absorption Spectrometry; ICP-AES, Inductively Coupled Plasma – Atomic Emission Spectrometry; ICP-OES, Inductively Coupled Plasma – Optical Emission Spectrometry; MP-AES, Microwave plasma- Atomic Emission Spectrometry; ICP-MS, Inductively Coupled Plasma - Mass Spectrometry

4 Conclusıon

In this study, the average of the concentration of copper in sheep's milk was higher than the cow's milk samples from regional farms in Harran lowland of Turkey. Differences in copper content of cow and sheep milk may be originated to feed, lactation period or the genus of the animals. This study showed that when sampling, the environmental factors such as feed, water, soil should be analyzed in terms of the copper element as well as milk samples whose geographical origins are known. Features studies with a large number of milk, feed, water, and soil samples, more representative of the geographical origin and of the species of milk producing, are recommended.

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