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Araştırma Makalesi

Analysis of Some Trace and Toxic Element Concentrations of Sheep Milk by Using an Inductively Coupled Plasma Optical Emission Spectrometer

Serap KILIÇ ALTUN[1*] Nilgün PAKSOY[2]

[1] Harran University, Veterinary Faculty, Department of Food Hygiene and Technology 63200 Şanlıurfa, Turkey.
[2] Harran University, Veterinary Faculty, Department of Biochemistry, 63200 Şanlıurfa, Turkey

***Sorumlu Yazar:**
skilicaltun@harran.edu.tr

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Abstract

In sheep farming, especially in extensive livestock systems, monitoring of trace and toxic element concentrations is important to determine the nutritional condition of animals, besides the nutritional importance of milk and the amount of potentially toxic element residues in dairy products. In this study, the concentrations of trace elements (zinc, copper, chromium, manganese, nickel, cobalt) and toxic elements (lead, cadmium) in raw sheep milk samples (n = 51) purchased from local markets in Şanlıurfa province were determined by ICP-OES. Zinc, copper, chromium, manganese, nickel levels in raw milk samples were determined as 4967.9±2968.2, 228.7±332.1, 155.8±39.3, 1180±30.4, 220±50,3 µg/L, respectively. Cobalt was found below the detection limit in milk samples. Generally, the levels of the trace elements were within the ranges reported in other studies in sheep milk. Lead was detected in all milk samples, with an average level of 0.11±0.03 µg/L, which was below the maximum limits set in the Turkish Food Codex. Therefore, it did not pose any risk for human consumption. Cadmium was determined at the level of 5.12 µg/L in only one sample. The maximum amount of cadmium allowed in the Turkish Food Codex Communiqué on Determination of the Maximum Levels of Certain Contaminants in Foodstuffs is 0.01-1.0 mg/kg for various foods and the value determined in this study is within the safe limits. As a result, it was determined that the sheep milk analyzed in this study did not threaten public health in terms of toxic elements, and the levels of trace elements were comparable with other study data.

İndüktif Eşleştirilmiş Plazma Optik Emisyon Spektrometresi Kullanılarak Koyun Sütünün Bazı Eser ve Toksik Element Konsantrasyonlarının Analizi

Özet

Koyunculukta, özellikle ekstansif besi sistemlerinde, eser ve toksik element konsantrasyonlarının takibi, hayvanların beslenme durumu ve ayrıca sütün besin değeri ve süt ürünlerindeki potansiyel olarak toksik element kalıntılarının miktarını belirlemek için önemlidir. Bu çalışmada, Şanlıurfa ilinde yetiştirilen koyunlardan elde edilerek lokal marketlerde satışa sunulan çiğ süt örneklerinde (n = 51) eser element (çinko, bakır, krom, mangan, nikel, kobalt) ve toksik element (kurşun, kadmiyum) konsantrasyonları ICP-OES ile belirlendi. Çiğ süt örneklerinde çinko, bakır, krom, manganez, nikel düzeyleri sırası ile 4967.9±2968.2, 228.7±332.1, 155.8±39.3, 1180±30.4, 220±50,3 µg/L olarak tespit edildi. Süt örneklerinde kobalt elementi deteksiyon limitinin altında bulundu. Genel olarak, eser elementlerin konsantrasyonları, dünya çapındaki koyun sütlerinde yakın zamanda yapılan diğer araştırmalarda rapor edilen aralıklar içindeydi. Süt örneklerinin tamamında kurşun tespit edilmiş olup ortalama 0.11±0.03 µg/L düzeyinde bulundu ve Türk Gıda Kodeksinde belirlenen maksimum limitlerin altındaydı. Bu nedenle insan tüketimi için herhangi bir risk oluşturmadı. Kadmiyum ise yalnızca 1 örnekte 5.12 µg/L düzeyinde belirlendi. Türk Gıda Kodeksi, Gıda Maddelerinde Belirli Bulaşanların Maksimum Seviyelerinin Belirlenmesi Tebliği'nde izin verilen maksimum kadmiyum miktarı çeşitli gıdalar için 0.01-1.0 mg/kg arasında olup bu çalışmada belirlenen değer güvenli sınırlar içerisindedir. Sonuç olarak bu araştırmada analiz edilen koyun sütlerinin toksik elementler bakımından halk sağlığını tehdit etmediği, eser elementlerin düzeyleri ise diğer çalışma verileri ile kıyaslanabilir olduğu tespit edildi.

Introduction

Milk is a biological liquid that is secreted from the mammary glands in order to feed the infant, and contains all the nutrients in its composition in a sufficient and balanced ratio for nutrition and growth (Paksoy, 2017). Sheep milk basically contains proteins mostly consisting of casein, essential fatty acids, lactose in disaccharide structure and many basic chemical components such as vitamins and minerals (FAO, 2017). Sheep milk is a food that people have benefited from for centuries, but in recent years, when functional foods have become widespread, sheep milk will play a very important role in providing benefits to human health (Mohapatra et al., 2019). Ovine milk and its products are also used for medical purposes, especially for babies (Haenlein, 2001). Although the medical importance of sheep's milk is increasing day by day, the number of studies in this field is limited. However, the requisition for sheep milk is growing in the global market. Sheep milk amounts to 36.5 of the world's total small ruminant milk production (FAO, 2017). Sheep milk, which constitutes 6.6% of the 22 million 960 thousand tons of milk production in Turkey according to 2019 TUIK data, makes significant contributions to the country's dairy industry (TUIK, 2019). Many researchers have reported that sheep milk has rich content in terms of essential elements (Zhang et al,,2006; Molik et al., 2008; Barlowska et al., 2011). Especially sheep milk ilk is a significant source of minerals, particularly calcium, phosphorus, potassium, magnesium, sodium, chloride and iodine (Mohapatra et al., 2019). The number of studies reporting the levels of elements such as copper, zinc, manganese, nickel, cobalt, cadmium, and lead in the composition of sheep's milk is quite low. However, trace elements such as copper and zinc are essential for many biological functions in metabolism. The lack of these trace elements conduces remarkably to the global disease charge; whereas, high concentrations of these trace elements can also have adverse health effects. The necessity and toxicity of elements vary from element to element and from species to species (Kazi et al., 2009). The possible harms of toxic elements in the composition of sheep's milk, which is a food whose importance for human health is increasing day by day, should also be investigated. At the same time, the diet of sheep is mostly grassland, so these animals may be considered as bio-indicators of the environment and their milk can be a helpful method to monitor environmental pollution (Llobet et al., 2003). Toxic elements like lead , cadmium, and nickel whose toxic effects are renowned (Mohapatra et al., 2019) are well deployed in the environment and small ruminants are subjected to their accumulation by ingesting feed, water, and grass (Pšenková and Toman, 2021; Rahimi et al., 2013; Najarnezhad and Akbarabadi, 2013). The aim of the presented study was to determine the concentration of some trace and toxic elements in sheep milk of Şanlıurfa province.

Materials and Methods

The material of this study consisted of 51 sheep's milk offered for sale in Şanlıurfa. Purchased raw sheep milk samples were placed in 50 mL polyethylene tubes frozen and stored in a deep freezer at -19 °C until analysis.

The digestion procedure of the milk samples, which was carried out with the aim of completely burning the organic content and dissolving the elements in the acid, was achieved by a 3-stage burning process in a CEM XPress brand microwave oven (Altun et al. 2018). For this purpose, all plastic and glass equipment to be used in both incineration and analysis were kept in 5% HNO3 and then rinsed with ultrapure water and dried. The milk samples, which were taken out of the deep freezer and brought to room temperature, were homogeneously pipetted into the teflon carriers of the microwave oven as 1 ml each. Then, 4 mL of HNO_3 (65% v/v) and 2 mL of H_2O_2 (30% v/v) were added to each teflon carrier, respectively;

Stage 1: 10 min at 120ºC 1600 Watts

Stage 2: 5 minutes at 180 ºC 1600 Watts

Stage 3: 20 min at 210 ºC 1600 Watt combustion was carried out at

The sample solutions, which were taken out of the microwave oven and cooled into the room temperature, were taken into 50 mL polyethylene tubes and their pH was increased above 1.0 by adding up to 50 mL of ultrapure water. The analysis of zinc, copper, chromium, manganese, nickel, cobalt, lead and cadmium elements in raw milk samples prepared for analysis was performed with ICP-OES (Optima 7000 DV Perkin-Elmer). The standard curve of the device was drawn with the lowest 1 µg/L and the highest 30 mg/L standard (Merck and Perkin Elmer) solution. Analysis of each sample was performed in the ICP-OES device in 7 minutes. In this study, the mean and standard deviation analysis of the samples were performed using the SPSS 11.0 (SPSS Inc., Chicago, IL, USA) package program.

Results

The descriptive numbers of zinc, copper, chromium, manganese, nickel, cobalt, lead, and cadmium values of 51 sheep raw milk sold in Şanlıurfa province analyzed with ICP-OES within the scope of the study are summarized in Table 1. Considering the element levels of the sheep milk samples used in the study are checked out it is seen that the concentration order of the trace elements examined is Zn>Mn>Cu>Ni>Cr and cobalt is below the detection limit. Although lead, one of the toxic elements, was found in all samples, it was determined that it was below the safe contamination limit determined for raw milk.

Table 1. Sheep milk trace and toxic element concentrations

Element	Positive sample number	Minimum	Maximum	Mean±SD
Zn (µg/L)	51	778	12650	4967.9±2968.2
Cu (µg/L)	45	9.82	1260	228.7±332.1
Cr (µg/L)	51	125	418	155.8±39.3
Mn (µg/L)	51	1150	1290	1180±30.4
Ni (µg/L)	51	86.4	290.2	220±50.3
Co (µg/L)	-	<LOD	<LOD	<LOD
Pb (µg /L)	51	0.018	0.203	0.11±0.03
Cd (µg/L)	1	5.12	5.12	-

Discussion

The mean concentrations of trace and toxic elements in sheep's milk are listed in Table 1. When we analyzed Table 1, it is prominent that the content of the toxic elements in the milk of this research was very low, below the LOQ limit except for lead. A similar status was stated in the research of Antunovič et al. (2005) that, normally, milk of sheep includes nominal concentrations of toxic elements. The level of toxic elements in milk is affected by factors such as environmental causes, feeding rations, and manufacturing processes (Anastasio et al., 2006). The average zincF level in the sheep milk analyzed in this study was 4967.9±2968.2 µg/L, and the data were similar when compared with the sheep milk collected from four different sites in southern part of Italy (Miedico et al. 2016). In a study conducted by Pšenková and Toman in 2020 in Western Slovakia with 30 sheep milk using ICP-AES method, zinc levels were found to be between 5.08±2.42 mg/L(Pšenková and Toman, 2021). The average data in this study is in line with our findings. The zinc levels (778-12650 µg/L) were also in agreement with those reported for sheep milk from Konya, Mardin, Şanlıurfa provinces of Turkey (1.52-6.68 mg/L) (Paksoy et al., 2018). Copper was qualified by a great variation comparatively with the data reported in the literature. Especially, the concentrations of copper in the this study were vaguely higher, in sheep milk samples (9.82-1260 µg/L), matched to the results acquired by Miediko et al.(2016) (41-1040 ng/g), comparable to that found by Ivanova (2011) (0.24-0.34 mg/L). In sheep milk of Bulgarian breeds (Tetevska and Strednostaroplaninska sheep), Gercthev and Mihaylova (2012) reported lower concentrations of copper (0.040 and 0.043 mg/100 g). Saber and El Hofy (2018) reported that the mean concentration of copper in sheep milk from Bedouin areas at El-Beheria governorates, Egypt, was 0.59±0.05 mg/L (Saber and El Hofy, 2018). The average chromium level of the sheep milk analyzed in this study was 155.8±39.3 µg/L, and the data were lower when compared with the chromium levels of Ile de France breed milk (0.290 mg/kg) collected from the Northeast part of Hungary (Póti et al. 2012). The concentrations of chromium analyzed in this study were higher than those described for fresh sheep milk of Karakachan breed, raised in the region of the Middle Rhodopes (0.05-0.06 mg/L) (Ivanova et al., 2011). The mean manganese level of the sheep milk analyzed in this study was 1180±30.4 µg/L, and the data were higher when compared with the manganese levels of sheep milk (89.6 ng/g) collected from the southern part of Italy (Miedico et al. 2012). Also mean manganese level of this study is higher than the mean level (0.016 mg/L) of Saber and El Hofy's study results. The mean concentration of nickel in sheep milk samples was 220±50.3 µg/L which was higher than the study reported by Pšenková and Toman (2021) for sheep milk (<0.1 mg/kg). Cobalt was found below the detection limit in this study. Low levels of cobalt in sheep milk samples were reported by Miedico et al. (2016) with a mean level of 3.88 ng/g. In this study, Candmium was found at the level of 5.12 µg/L in only one milk sample. Concentrations of lead and cadmium in this study were lower than those reported by Poti et al. (2012) (0.023 mg/kg and 0.012 mg/kg). Additionally, Pšenková and Toman (2020) reported lower mean lead and cadmium concentrations (<0.1 mg/kg and <0.04 mg/kg) from western Slovakia. The lead concentrations were in agreement with those reported for sheep milk samples from Iran (12.1 ng/mL) (Rahimi et al., 2013).

Conclusions

The levels of trace elements disclosed mean concentrations comparable to the other reported research in the world. The concentrations of these elements require further studies in sheep milk and dairy products. It was determined that the cadmium and lead amounts of sheep milk determined in this study did not exceed the maximum allowed in the Turkish Food Codex, Communiqué on Determination of the Maximum Levels of Certain Contaminants in Foodstuffs and were within safe limits.

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