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HEAVY METALS LEVELS IN GOAT MILK OF THE MEDITERRANEAN REGION OF TURKEY

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ABSTRACT

Concentration of the essential elements as Zn and Cu and potentially toxic elements as Pb, Cr and Cd in goat milk samples from two different farming systems were measured, to assess whether the toxic and essential elements are within recommended levels. Quantitative analysis of Cd, Cr, Cu, Pb and Zn were performed using an atomic absorption spectrophotometer. Toxic heavy metals from intensive and extensive farms for Pb and Cd were found 0.187, 0.038 and 0.019, 0.037 ppm, respectively while essential metals such as Zn, Cu and Cr were 0.641, 0.533; 0.168, 0.093 and 0.021, 0.023 ppm, respectively. No significant differences were found for Cr ($P > 0.05$) among the two farms while Pb, Cu, Zn and Cd were differed statistically significant ($P < 0.05$). Further investigations of heavy metal levels in milk in a greater number of farms from Mediterranean region of Turkey are necessary to determine the situation more profound.

Key words: *Goat milk, heavy metals, essential elements, Turkey*

INTRODUCTION

Rapid urbanization, technological improvement, growing population, industrial development and increased roadway traffic have caused a significant increase in environmental contamination and heavy metals contamination have been treating human health as transmitting into human body via food chain. Heavy metals occur as natural constituents of the earth crust, and are persistent environmental contaminants since they cannot be degraded or destroyed. To a small extent, they enter the body system through food, air, and water and bio-accumulate over a period of time (**Lenntech, 2004**). As trace elements, some heavy metals such as Cu and Zn are essential to maintain the metabolism of the human body while Pb and Cd are nonessential minerals that are of direct concern to human and livestock health and may accumulate in the body, particularly in the kidney, liver, and to a lesser extent in the muscle (**Li *et al.*, 2005**). With increasing environmental pollution a heavy metal exposure assessment study is necessary (**Barbera *et al.*, 1993; Schuhmacher *et al.*, 1993; Ikeda *et al.*, 1996; Raghunath *et al.*, 1997**) .

The toxic metals content in milk and dairy products can be due to; environment or manufacturing process steps. Turkey, with 6.7 million heads of goat, 25 million heads of sheep and 11 million heads of cattle represents an important source for dairy processing industry (**FAO, 2007**). Mediterranean region of Turkey with nearly 2 million head of goats represents an important source of income for rural areas in this territory. The goat milk is almost used for cheese processing industry. At present no data are available concerning levels of heavy metals concentration in goat milk produced in the Mediterranean region of Turkey. Among other fluids, milk can be a good indicator of the status of certain mineral elements and levels of certain mineral elements in milk are of value for the determination of deficiency or toxicity status, although individual variability can be very high and external contamination provides problems for certain trace elements status evaluation (**Khan *et al.*, 2006**). Milk composition can be related to nutritional supply, therefore, milk minerals profile can be an appropriate tool to evaluate trace minerals nutritional status of dairy sheep and goats (**Greppi *et al.*, 1995**). The aim of this study is to detect the heavy metals concentrations in goat milk collected from two different farms representing intensive and extensive systems in Eastern Mediterranean Region of Turkey.

MATERIALS AND METHODS

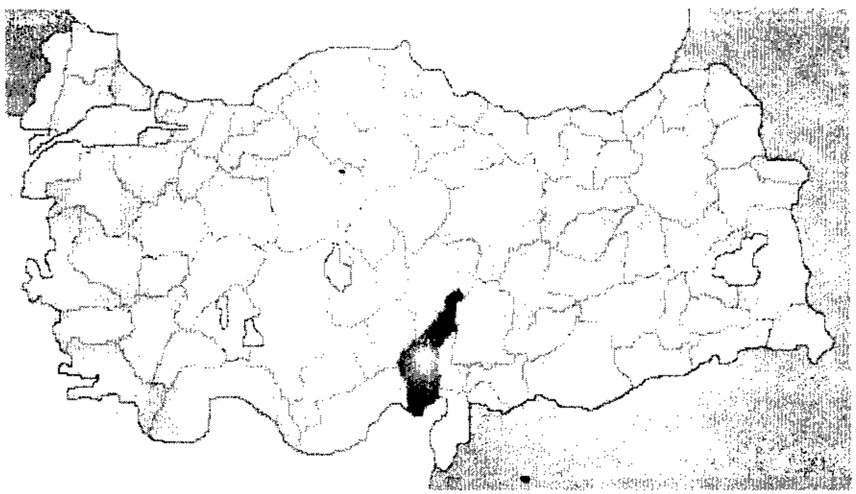

Figure 1. Map of the study area (Adana province)

Milk samples were taken for mineral analysis five times fortnightly from mid-lactation to mating time from lactating goats. Samples of milk were collected in 125ml nalgene bottles. The samples were stored at 4°C until they were transferred to the Chemistry Laboratory at University of Cukurova for chemical analysis. Samples of milk for analytical preparation were first dried overnight in an oven at 60°C and then ashed overnight in a muffle furnace at 550 °C. Ash was solubilized by digestion, first with 50% nitric acid, secondly with 10% nitric acid and finally with distilled water using the technique described by **Miles et al. (2001).** Solutions were filtered, diluted to appropriate detection level and analyzed by Atomic Absorption spectrophotometry for

Pb, Cu, Zn while Cr, Cd ions did not detected by Atomic Absorption Spectroscopy so ICP was used for determination of them. Portions (2 g) of milk samples were dry ashed in a porcelain crucible, solubilized in 10 ml 6M HCl, quantitatively transferred into 25 ml volumetric flasks, and diluted to volume with double-deionized water.

Statistical analysis

At the end of the experiment, data of trace minerals (Pb, Cu, Zn, Cr, Cd) in milk samples from two different farms were analyzed by Student-*t* test. Means differences were considered significant at $P<0.05$ level. Data are presented as mean ± standard error **(SPSS 10.0 version, 1999)**.

RESULTS AND DISCUSSIONS

The values of Pb, Cu, Zn, Cr and Cd in both intensive and extensive farms' milk were given in Table 1. The general mean values of the examined elements in raw milk is reported as; Pb 0.02 ppm., Cu 0.48 ppm, Zn 0.46 ppm., Cr 0.77 ppm., Cd 0.63 ppm. **(Güler, 2006)**.

Table 1. Levels (ppm) of Pb, Cu, Zn, Cr and Cd in goat milk from two different farms in Adana.

Heavy metals	Turkish Food Codex	Intensive enterprise	.Extensive enterprise	P
Pb (ppm)	0.02	0.187 ± 0.0348 [a]	0.038 ± 0.0224 b	*
Cu (ppm)	0.48	0.168 ± 0.0098 [a]	0.093 ± 0.0106 b	*
Zn (ppm)	0.46	0.641 ± 0.0321 [a]	0.533 ± 0.0435 b	*
Cr (ppm)	0.77	0.021 ± 0.0051	0.023 ± 0.0060	NS
Cd (ppm)	0.63	0.019 ± 0.0043 [b]	0.037 ± 0.0008 a	*

[a, b] Means within row with different superscripts differ significantly. * $P<0.05$, NS: not significant

While the concentration of "toxic" metals (Pb), in samples from the intensive enterprise were found higher than that from the extensive farm , Cd and Cr levels were found lower. Lead is one out of four metals that have the most damaging effects on human health. It can enter the human body through uptake of food (65%), water (20%) and air (15%) **(Lenccht, 2004)**. The differences in Pb, Cu, Zn and Cd between the two enterprises were found significant ($P > 0.05$). Although the mean values of Cu, Cr, and

Cd levels in the present study were lower than those in the Turkish Food codex, Pb and Zn levels were markedly higher.

This study shows that, in milk from the two different enterprises in Adana, there are highest concentrations only of Pb among the "toxic" metals. Besides, in all samples studied Pb measured to be in dangerous concentrations. Maximum limit (0.02 ppm) of toxic Pb element in milk was stated in the **Turkish Food and Codex (1997).** The contents of cadmium in milk have not been published in the Turkish Republic yet. **Rodriguez et al. (1999)** reported 0.0184 ppm as the maximum content of Cd and 0.04 for Pb in raw milk, while in this study the average contents were 0.019 ppm for Cd and 0.187 ppm for Pb in intensive enterprise. The presence of Pb in milk samples could be due to various factors: transhumance along roads and/or motorways, fodder contamination, climatic factors, such as winds, and the use of pesticide compounds **(Licata, 2004)**. Pb levels (0.13-0.50 ppm) were within the range of values reported by **Guler *et al.* (2000)**.

Table 2. Minimum and maximum values of metals measured from the two different farms.

	Intensive			Extensive		
	Max	Min.	M± SD	Max	Min.	M+SD
Pb	0.50	0.13	0.187 ± 0.0348	0.38	0.13	0.038 ± 0.0224
Cu	0.30	0.10	0.168 ± 0.0098	0.23	0.05	0.093 ± 0.0106
Zn	0.86	0.37	0.641 ± 0.0321	0.89	0.21	0.533 ± 0.0435
Cr	0.06	0.02	0.021 ± 0.005	0.07	0.03	0.023 ± 0.0060
Cd	0.04	0.03	0.019 ± 0.0043	0.04	0.02	0.037 ± 0.0008

On the contrary to Pb, Cd levels have been found lower in the samples than levels declared by the **Turkish Food Codex (1997)** which shows that there are no Cr and Cd-related toxicological risks in Adana. While Cu levels were found lower, Zn level was measured high from the samples collected from both enterprises. **Güler (2006)** found that Cd and Pb levels in goat raw milk were 0.63 and 0.06 ppm, respectively. Results of the present study were found lower than those reported by **Güler (2006)** and Pb values were in agreement with **Anastasio *et al.*(2006)** while Cr levels (0.06-0.40 ppm) were found higher than the present results (0.021-0.023 ppm).

Different results from various researchers are set on Table 3. Results show different levels of the metals are being measured by the researchers. These differences could be due to previous use of parasiticides, fertilizers, industrial pollution, heavy traffic regions and environmental conditions.

Table 3. Concentrations of heavy metals in milk samples with relative references

Concentration (µg/kg w.w.)	References								
	Baldini *et al.*, 1990	Wojcicchowska-Mazurck *et al.*, 1995	Campillo *et al.*, 1998	Cerutti, 1999	Triphathi *et al.*, 1999	Alais, 2000	Simsek *et al.*, 2000	Tiecco, 2000	Martine *et al.*, 2001
Toxic metals									
Pb	4– 50 (14.2)	25– 47 (36)		n.d.– 1500	1,7	50– 1000	18– 49 (33.5)	120– 15,800	1,8
Cd	0.2– 1.9 (0.52)	2 – 10 (6)		n.d.– 20	0.07	20– 30			0.47
Essential metals									
Cr	< 10			10-700		30			1,1
Cu	40-630 (174)	120-280 (200)	462	50-200	43.2	200-300	390-960 (675)	< 2000	60
Zn	3300-7300 (4800)	24.000-39.000 (31.500)	28.000	300-6000	3177	3000-6000	3770-5010 (4390)	4000-5000	3800

CONCLUSIONS

Results of the present study indicate the danger of lead excess in milk produced in Adana Province located in the Mediterranean region of Turkey. One of the greatest concerns in the last years is to establish the security and safety in food chain due to the fast industrialization and environmental pollution in the World. That is necessary not only for foods but also for milk and dairy products. Additionally, our data has a particular importance not only for their significance but because they were measured in Adana province with a very high risk of environmental pollution due to the high industry and agricultural activities, especially horticulture. Further studies are necessary to evaluate the heavy metal contents from various farms in order to determine the potential of toxicological risks in milk and dairy products.

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INTRODUCTION

Flavour is considered a major attribute that influences the selection and consumption of cheese. With the increased attention to produce cheese from goat's milk and resolving of some problems associated with goat's milk cheese, especially goaty flavour, have become economically more important. The general consensus among researchers is that mixtures of alkanoic acids with short chain from C 2 to C 10 seem to have a major effect on the flavour of cheese (**Bading and Neeter, 1980; Law,1982; Woo *et al.*, 1984 and Scott ,1986**). Although n-chain fatty acids are abundance, certain volatile branched chain fatty acids exhibited characteristic flavours at very low concentrations.

Probiotic organisms such as ***lactobacillus*** and ***bifidobacterium spp.*** are described as living microorganisms, which upon ingestion in certain numbers exert health benefits. **Rasic and Kurmann (1983)** had shown that such organisms have several health benefits for human e.g, anticarcinogenic effect, increased immuno competence and antimicrobial activity. Meanwhile, **Blanchette *et al.*, (1996)** showed that dairy products containing bifidobacteria may be tolerated by individuals who are suffering from lactose intolerance.

Manufacturing of low fat cheese may be useful in overcoming the goaty flavour problem. However, the manufacture of low fat cheese is accompanied by some technological problems such as lack of typical flavour and inferior body and texture characteristics.

To obtain an attractive texture in reduced-fat cheese, most commonly, water and/or whey are used to replace the fat in filling up the three dimensional casein network. Sometimes, different water-holding agents like salt or whey proteins are added to stabilize the structure. Increasing the content of whey proteins in low fat cheese using UF techniques, lead to a smoother consistency of the low fat cheese, an increase in cheese yield and an accurate moisture content of the cheese **(de Boer and Nooy, 1980).**

The use of attenuated bacterial cells which release enzymes to act freely in the cheese represents one of the most important effort to improve the flavor of low fat cheese. Bacterial cells may be attenuated by freezing, heating or chemical treatments for the purpose of temporarily inactivating them metabolically but not actually killing them. The technique of using bacterial cells attenuated by heat treatment to preserve the desired enzyme activities is used successfully for reduced fat cheese **(Ardo *et al.*, 1989 Ardo, 1994 and Skeie *et al.*, 1995).** The bacterial enzymes are kept entrapped in these heat-treated membranes during cheese manufacturing and leak into the cheese during early ripening.

Ardo *et al.* (1989) and Ardo and Mansson (1990) had active work in this field and had developed a system using heat treated lactobacilli to give a desirable aroma in low-fat cheese. The heat shocked lactobacilli released their amino peptidase early