



RESEARCH ARTICLE

Investigation of some heavy metal presence in the milk of cattle

Gülçin Algan^{1*}, O. Cenap Tekinşen², Veli Gök³

Özet

Algan G, Tekinşen OC, Gök V. İnek sütlerinde bazı ağır metal varlığının araştırılması. *Eurasian J Vet Sci*, 2012, 28, 3, 159-163

Amaç: Bir besin kaynağı olan sütte toksik metaller üzerinde çok fazla araştırma bulunmamaktadır. Bu çalışmada Konya yöresinden elde edilen inek sütlerinde bazı ağır metallerin varlıkları araştırıldı.

Gereç ve Yöntem: Konya yöresinde 19 yerleşim biriminden alınan toplam 61 adet süt numunesinde kurşun (Pb), kadmiyum (Cd), arsenik (As) selenyum (Se) ve çinko (Zn) miktarları Atomic Absorption Spectrometer ile araştırıldı.

Bulgular: Kurşun, kadmiyum, arsenik, selenyum ve çinko düzeyleri sırası ile 0.0000001, 0.0000388, 0.0000839, 0.0000331 ve 0.0026681 ppm olarak belirlendi.

Öneri: Belirlenen kurşun, kadmiyum, arsenik, selenyum ve çinko düzeyleri Birleşik Gıda Kodeksinin besinler için önerdiği maksimum düzeylerin çok altında bulundu. Bu düzeylerin insan sağlığı için tehlikeli boyutlarda olmadığı ve süt inekleri için kontaminasyon riskinin de yüksek olmadığı kanısına varıldı. Araştırmalara daha çok sayıda örnek alınarak ve daha fazla element çeşidini konu alarak devam edilmelidir.

Abstract

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Aim: There was no enough research about the presence of heavy metals in the milk a source of important nutrients. In this study, some heavy metal existence was investigated in the milk obtained from Konya region.

Materials and Methods: Lead (Pb), cadmium (Cd), arsenic (As), selenium (Se) and zinc (Zn) levels of 61 milk samples obtained from 19 places in Konya region were determined by Atomic Absorption Spectrometer.

Results: Average lead, cadmium, arsenic, selenium and zinc levels were 0.0000001, 0.0000388, 0.0000839, 0.0000331 and 0.0026681 ppm, respectively.

Conclusion: Determined lead, cadmium, selenium, zinc and arsenic levels are much below the maximum levels recommended by Joint Food Codex. These levels are not a threat against human health and the contamination risk for dairy cattle is not high. Further research needs to be conducted by taking more samples and studying more element types.

¹Vocational School of Health Services Child Development Program, ²Department of Food Hygiene and Technology, Faculty of Veterinary Medicine, Selçuk University, Campus, Konya, ³Department of Food Engineering, Faculty of Engineering, Afyon Kocatepe University, Campus, Afyon, Turkey
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*gulcin8751@hotmail.com

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► Introduction

Heavy metals increasing in amount due to the polluted environment have become one of the major contaminants and turned into the sources of contamination that threaten our environment. Natural resources (air, soil, water) are likely to be polluted by metals. Contaminators in the atmosphere can be transferred to far distances through air currents and other atmospheric conditions. Falling down on the earth surface in time, they pollute vast land and water areas and this also leads to the contamination of animal products and seafood (Baysal 2004). Nisbet et al (2010) reported that the average value of metal concentrations in fish samples were determined as follows: 2.38 µg/g for copper, 5.41 µg/g for manganese, 26.06 µg/g for iron, 3.40 µg/g for nickel, 25.74 µg/g for zinc, 0.77 µg/g for lead and 0.022 µg/g for cadmium, but mercury was not detected. Industrial based inorganic compounds such as cyanide, copper, mercury, lead, cadmium, arsenic which are included in wastes in water supplies and detergents, chemical fertilizer and pesticide wastes resulting from agricultural applications are the substances which are resistant to natural dissolution (Baysal 2004). Contamination of soil by heavy metals might be resulting from dissolution of the rocks including heavy metals due to various reasons and being transferred into water and soil (Vanlı and Yazgan 2008). Heavy metals contaminating the foodstuffs within the environmental cycle reach the human body through food chain (Kahvecioğlu et al 2004). It is inevitable to be affected by the heavy metal contamination for the plants and animal products which set up the foundation of food chain and biological cycle (Zengin and Munzuroğlu 2004, 2005). Therefore, these heavy metals that are taken into body through consumption of the contaminated foodstuffs are likely to cause health problems that might even result in sudden deaths depending on their concentration and quantity of remaining inside the body (Kahvecioğlu et al 2004). There aren't many studies related to the toxic metals in milk, which is one of the important food sources in our country.

The purpose of this study is to determine various heavy metals that can contaminate milk "the main food resource", and the possible sources of contamination.

► Materials and Methods

In the research, 61 milk samples that were produced for sale in dairies and family – household type – enterprises were collected from different enterprises

in nineteen settlements in the center of Konya and its towns (Akbel, Aksaray, Beyşehir, Çevreyolu, Derbent, Güney sınır, İçeriçumra, Kadınhanı, Karatay, K. Kumköprü, Lalebahçe, Mengene, Sedirler, Saraçoğlu, Ş. Karaağaç, T. Karaaslan, U. Harmanlar, Yağlıbayat, Yaylapınar). These enterprises were chosen carefully by taking into consideration if there were any highways or industrial establishments near the places where animals were kept (cowshed or grassland) or milk was produced. Minimum 200 mL sample taken from different parts of milk containers were kept at -18 °C in order to get a homogeneous mixture. Glass jars used for samples were kept in 1:1 HNO₃ solution for one night and they were dried and used after they were washed with distilled water first and then washed again with bidistilled water. Heavy metal contents of milks were measured by Atomic Absorption Spectrometer (Javed et al 2009, Aslam et al 2011, Bilandzic et al 2011). The choice of sample preparation method mostly depends on the analysis method to be used and on the element to be examined. Accordingly, dry-ashing process was performed for lead analysis and wet-ashing was used for the analysis of cadmium, arsenic, selenium and zinc (FAO 1980). Separate solubilization was performed for each sample and then Cd, Pb, Se, As and Zn quantities in the samples were measured by AAS. For the Analyses; APDC solution (2%); 2 g APDC was dissolved in 100 mL bidistilled water. Free acid and impurities were removed by extracting 10 ml butyl acetate 2-3 times. Citric acid solution (10%): 10.0 g lead-free citric acid was dissolved in 100 mL bidistilled water. Lead impurities were removed if necessary. Bromo-cresol indicator (0.1%): 0.100 g Bromocresol green, sodium salt at 3.8 (yellow), 5.4 (blue) pH range was solved in 100 mL water. 1 mL was used for 10 mL analytical solution. Butyl acetate: was saturated with water and then used. 1 N HNO₃: 138 mL nitric acid was added to 500 mL bidistilled water and completed to 2 liters. While Pb, Cd, Se and As measurements were directly made with this solution, Zn measurements were carried out after 2 mL sample taken from this solution was diluted to 10 mL.

Mann-Whitney-U test was used to compare the heavy metal contents of the samples taken from the settlements with the aim to present the interregional differences and to determine the mean values of the results from the research. $p < 0.05$ was accepted statistically significance level (SPSS 10.0).

► Results

Heavy metal levels are shown in Table 1.

Table 1. Heavy metal concentrations determined by flame AAS in raw milk samples (ppm, median).

Lead	Cadmium	Arsenic	Selenium	Zinc
0.0000001	0.0000388	0.0000839	0.0000331	0.0026681

► Discussion

It was determined that lead content of the tested milk samples was at very low levels (on average 0.0000001 ppm, Table 1). When Pb amounts of samples were compared with each other, it was seen that heavy metal contents of the milk samples collected from towns were higher than those collected from the city center ($p < 0.05$). Silva et al (2011) examined Pb concentration of 23 fodder samples in a study they made on the lead poisoning in dairy cattle in Pernambuco region of Brazil. Pb concentrations in the samples ranged from 5 to 344 mg/kg. It was reported that the measured Pb level exceeded the permissible maximum level and there was a high risk of contamination for the dairy cattle. In another research, Pb content values of the milk samples examined in Yugoslavia were found to be between 0.00 and 0.02 mg/kg. The Pb content measured in the study was higher than this study and lower than those measured in Brazil and Nigeria (average Pb 0.53 mg/dm³) (Lawal et al 2006). Bilandzic et al (2011) studied Pb concentration in raw cow's milk in southern and northern regions of Croatia and found 58.7 µg/L and 36.2 µg/L, respectively. It was seen that Pb content of the samples taken from both regions exceeded the highest recommended level. When the studies were examined, it was seen that lead amounts of the milk samples in this present study were at a rather low level. This low Pb content probably resulted from being away from the traffic areas where leaded petrol was used. In a study conducted in an urban area, Yoon et al (2006) examined the transfer of lead from cars to fodder and they reported that Pb concentration in the dry matter was at a high level and exceeded the limit of (5-344 mg/kg). If, under normal conditions, milk doesn't have any contact with the lead material during processing and production, lead contamination does not take place. Lead is a contaminant which mostly comes from environment and it exists almost in all industrial environments. Lead in dumped waste can be transmitted to humans through water and food (Baysal 2004). As reported by Ekşi (1981), a high dose of lead was identified in the meat and milk of the cattle grazing on the fields around iron-casting workshops. The amount of lead decreased as the distance grew. The maximum acceptable limit of lead levels in foodstuffs were reported as 0.1-2 mg/kg by the Food Codex and the weekly intake per body weight was determined to be 0.05 mg/kg (FAO-WHO 1984). According to the Turkish Food Codex Communiqué concerning the Maximum Limits for Contaminants in Food Substances, Annex-4 Heavy Metals, Pb content in raw milk was reported to be 0.02 mg/kg (TFC 2008). Findings of the research, therefore, are below the acceptable level. The fact that Pb amount level was low in the milk samples analyzed in this study indicated the state of being away from an industrial area.

Cd amount in the milk samples examined was found

on average to be 0.0000388 ppm. When Cd levels in samples were compared with each other, it was found that heavy metal contents in milk samples collected from towns were higher than ($p < 0.05$) those collected from the city center; yet there wasn't a statistically significant difference between the samples ($p > 0.05$). Licata et al (2004) and Triphathi et al (1999) found 0.0228 and 0.00007 mg/L Cd in cow's milk respectively. Javed et al (2009) examined heavy metal residues in goat's and cow's milk during winter season and found that the levels of Cd (0.084) in goat's milk was higher than in cow's milk. Cd content of the milk samples in Nigeria (0.02-0.06 mg/day) was found to be higher than the recommended amount of nutrition (0.257 mg/L) (Lawal et al 2006). The average cadmium content in milk was found on average to be 0.00047 ng/mL by Licata et al (2004); and Azcue et al (1988) and Onianwa (1999) identified it to be 0.01 µg/g and 0.006 ppm, respectively. Turkish Food Codex reported that maximum permissible amount of cadmium in foodstuffs was 0.01-1.0 mg/kg for various foods (TFC 2002). When findings of this study were compared to the literature, it was seen that Cd content was too low. However, it shouldn't be ignored that the level of cadmium, is likely to go up depending on the growing environmental pollution and it can be a source of danger for both human and animal health.

Average arsenic amount in the milk samples examined in the study was determined to be 0.0000839 ppm. When As levels in samples were compared with each other, it was found that milk samples collected from towns had more As ($p < 0.05$) than those collected from the city center; yet there wasn't a statistically significant difference between the samples. The maximum acceptable limit of arsenic amount in foodstuffs is 0.1-2 mg/kg and the daily intake per body weight is 0.05 mg/kg (FAO-WHO 1984). Depending on the findings of the study, it is possible to suggest that As amount is not so high. It was noticed that As amount of the samples taken from different centers varied from time to time. This variation is believed to possibly result from artificial fodder and oil-cake used in animal nutrition. Bilandzic et al (2011) found the arsenic content of the raw milk collected from southern and northern regions of Croatia to be ranging from 283 µg/L to 1019 µg/L. Aslam et al (2011) examined the uptake of heavy metal residues from sewerage sludge in the milk of goat and cattle in summer season. As concentration in goat's milk 0.403 mg/L was found to be 0.078 mg/L higher as compared to cow's milk. Transmission from sewerage water used for agricultural purposes to the soil was reported as the reason for high level of heavy metal residues. When the related studies were examined, it can be said that As contents in this study remained at lower levels.

Findings of the study indicated that milk samples contained a pretty small amount of Se (on average 0.0000331 ppm, Table 1). When the samples were

compared with each other based on the settlements, it was found that samples from towns contained more Se than those taken from the city center ($p < 0.005$). Yet the difference between the samples was not statistically significant ($p > 0.005$). 0.04 mg/kg Se was found in fresh milk by Lante et al (2004) while Garcia (2006) identified 0.013 mg/kg and 0.23 mg/kg, respectively. Se content in this present study remained at very low levels when these values were examined. Selenium exists in the soil in the form of organic and inorganic compounds. Few of them are in the soluble form. Some plants can accumulate the selenium in the soil within their own structure and some even need selenium for their development. Therefore, the actual danger for humans and animals are the plants containing selenium in their structure. It is thought that plants in the regions of the towns where cattle graze do not accumulate selenium.

In the milk samples analyzed, the amount of Zn ranged from 0.0001588 ppm to 0.0114294 ppm and was found to be 0.0026681 on average (Table 1). It was seen that, as compared to towns, raw milk samples taken from the settlements in the city center indicated a considerable level of Zn and the difference was statistically significant ($p < 0.05$). When it was considered that the maximum level for the Zn amount in the foodstuffs was determined to be 5 mg/kg and the acceptable amount of zinc intake per body weight was determined to be 0.3-1.0 ppm by FAO-WHO (1984), Zn amount in the raw milk samples used in this study remained below the acceptable limits. While gathering milk samples for the study, it was seen that most of the milk was kept in the milk buckets made of galvanized iron for quite a while after milking process. IDF/FIL (1978) suggested that using storing tanks and milk buckets made of galvanized iron might increase the amount of Zn in milk. Maas et al (2011) examined 61 raw cow's milk to determine the transmission of heavy metal to milk. Zn content was found lower in raw milk than in cheese. In their studies Giri et al (2011) found lower levels of Zn concentration in milk (4.77 mg/L) as compared to other studies. While Enb et al (2009) found the Zn level in the milk of farm animals in Egypt to be 2.828 mg/L, Lante et al (2004) found 4.631 mg/L. Zn findings of the present study were much below the Zn amounts that Jusikiewicz et al (1983) detected in cow's milk (4.4 mg/kg). It was noticed that Zn contents of this study were at lower levels than those found in the related studies. Zn content found in the research was in parallel with the findings (<2.6 ppm) of Orlando et al (1998).

► Conclusions

Although the amounts of heavy metal determined in the samples were below the maximum values which were set by Joint Food Codex, it was noticed that these amounts increased due to some contaminations. It is possible to say that milk produced in Konya region hasn't been exposed to a serious contamination by

toxic metals such as Pb, Cd and As. Because the cattle are not put out to pasture in the center of Konya, they are fed with artificial fodder in cowsheds, whereas the cattle are pastured on meadow grass in the towns. An increase is likely in time in the heavy metal contents of the milk of cattle fed in the regions suffering from heavy traffic and environmental pollution. Further research needs to be conducted by taking more samples and studying more element types. Studies can be made on yearly and seasonal basis.

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