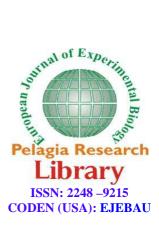
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Evaluation and determination of toxic metals (Lead and Cadmium) in cow milk collected from East Azerbaijan, Iran

Abolfazl. Asadi Dizaji¹, Ali. Eshaghi², Abolfazl. Aghajanzadeh Golshani¹, Kambiz. Nazeradl¹, Ali Asghar. Yari¹, Soheil. Hoda³

¹Department of Animal Science, Shabestar Branch, Islamic Azad University, Shabestar, Iran ²Department of Physico Chemistry Razi Vaccine & Serum Research Institute, Karaj, Iran ³Young Researchers Club, Shabestar Branch, Islamic Azad University, Shabestar, Iran

ABSTRACT

Milk has been considered as one of the unique sources for children and even adults nutrition. In this study was 100 milk samples collect from different zonal east Azerbaijan Province: Tabriz, Sarab, Maragheh, Meyaneh, Azarshahr, Oskou, Malekan and Ahar. In accordance with the present survey and studies the amount and level of Pb and Cd has been specified in the cow milk. In order to measure the poisonous metals of milk, four digestion methods have been experienced. Organic matter is digested with nitric acid, hydrogen peroxide and perchloric acid; the most suitable acids in wet digestion of milk. The dosage Pb and Cd in milk was accomplished with the help Spectrometry of atomic absorption using a Varian AA220 atomic absorption spectrometer (Australia). The highest concentration of cadmium was found in the Sarab city (4.52 ± 0.82 pbb) and the lowest ones in the Malekan city (0.57 ± 0.15 pbb). The highest concentration of Lead was found in the Meyaneh city (182.08 ± 20.25 pbb) and the lowest ones in the Ahar city (12.82 ± 1.91 pbb). Statistical analyses showed that there are significant differences between lead and cadmium concentrations in raw cow's milk samples from different regions of East Azerbaijan province. In all the samples measured cadmium contents, was less than authorized limit by FAO/WHO standard (Cd: $10\mu g/kg$). But only in 28% the samples measured Lead contents, was less than authorized limit by FAO/WHO standard (Pb: $20\mu g/kg$). The consequences have shown us that Lead and Cadmium causes dangerous effects on human organs, and we should do our best to decrease the amount of the above-mentioned metals.

Keywords: Metals, Milk, Toxicity, East Azerbaijan.

INTRODUCTION

Good quality measurements are essential to control and maintain products and processes quality, both in manufacturing, trade and in research. Milk is a primary source of nutrients in diets all around the world [2]. Milk products are a very important human nutrient since their consumption has increased in recent years. These products are also a good source of calcium and there biodisponibility is high. Increasing industrialization has been 261

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accompanied throughout the world by the new distribution of mineral substances from their natural deposit. Many of these have undergone chemical changes and finally pass, finely dispersed and in solutions, by way effluent sewage, dumps and dust, into the water, earth and the air and thus into the food chain.

By their spread speed in biosphere and increasing concentrations heavy metals are considered to be among the most hazardous pollutants [21]. The almost ubiquitous presence of some metal pollutants, especially cadmium and lead, in the environment facilitates their entry into the food chain, thus increasing the hazard of human and animal health [11].

With attention to damages due to dietetic absorption of lead and cadmium, such as disorder in operation of kidney and liver, increasing cordial-coronary disease, anemia, decreasing pregnancy, and most important, increasing spontaneously metal absorption and being one of the important selective food to nourish infants and other age groups.

Inorganic or aggregated forms of chemical substances (metalloids, heavy metals etc.) in feed and food represent a severe risk for their long-term toxicological effects. Contamination with heavy metals origin from human activities. Heavy metals insert to human food cycle together milk and Dairy Products. Heavy metals are widely dispersed in the environment. The toxicity induced by excessive levels of some of these elements, such as chromium (Cr), cadmium (Cd), lead (Pb) and mercury (Hg), are well known [12].

The toxic metal content of milk and dairy products is due to several factors in particular environmental conditions, the manufacturing process and the possible contamination during several steps of the manufacturing processes.

For carrying out these determinations were used different techniques: flame atomic absorption spectrometry [10, 16], capillary zone electrophoresis Suarez-Luque *et al.*, 2007[22], inductively coupled argon plasma emission spectroscopy [15], differential pulse anodic stripping voltammetric technique Tripathi *et al.*, 1999[23], inductively coupled plasma optical emission spectrometry [9], flow injection spectrometric methods [14], atomic fluorescence spectrometry [3] and stripping potentiometry [13].

East Azerbaijan Province Iran with more than 1.000.000 cows represents an important source of income for rural areas of this territory. The milk from cow is almost entirely used to drinking and produce yogurt. The aim of the study was to determine lead and cadmium concentrations in cow's milk collected in raw milk from the East Azerbaijan.

MATERIALS AND METHODS

Sampling: Raw milk was collected in winter (March and April) of 2010 in several zones of East Azerbaijan (Figure 1).



Fig1- Map of milk samples collection.

In this study was 100 milk samples collect from different zonal east Azerbaijan Province: Tabriz, Sarab, Maragheh, Meyaneh, Azarshahr, Oskou, Malekan, , and Ahar.

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The routine tests for dry substance, ash, pH, acidity and fat were accomplished according to the national standard (STR). The evaluation of the total protein nitrogen (TPN) and the nonprotein nitrogen (NPN) was based on the kjeldhal method, after the appropriate fractioned precipitation (Table 1).

For determination pb and Cd metals was used according to the AOAC (1990) methods [1].

Precautions against contamination

Plastic containers and all other laboratory ware used were new and were cleaned by soaking them for 24 h in the bath containing 10% HNO₃ solution and for 24 h in ultra pure water. After rinsing with ultra pure water they were dried in a class 10 clean bench Valiukenaite *et al.*, 2006[24]. From the final solution there are determined through chemical methods, according to STR: Pb and Cd. For the spectrometry of atomic absorption the hydrochloric solutions are preferred, because the metals halogenure are volatile in flame. Both for the verification of the reproducibility of the results, and for the better conservation of metals present in the traces, most of the milk samples were decomposed by wet way according to STR 8342/89, by incineration and calcinations at 500°C, is finally dissolved in Hcl 5N.

The dosage Pb and Cd in milk was accomplished with the help Spectrometry of atomic absorption using a Varian AA220 atomic absorption spectrometer (Australia). Operating conditions for the instrument show in table 1.

Table1- Operating conditions for t	the instrument
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	Pb	Cd
Wave length	228.8nm	283.3nm
Lamp intensity	75%	75%
Sample volume	20µ1	20 µl
Band pass	0.5nm	0.5nm
Sensitivity	0.56pg	1.5pg
Background correction	Yes	Yes

RESULTS AND DISCUSSION

In table 1 there are presented some physicochemical characteristics of the collected milk from the region of East Azerbaijan from year 2011.

Table 1- composition characteristics of milk from the region of East Azerbaijan from year 2011

Sample of milk	DM	TPN	NPN	Fat
Tabriz	11.25	3.09	0.112	3.5
Sarab	11.70	3.29	0.130	3.5
Maragheh	11.28	3.16	0.116	3.0
Meyaneh	10.91	3.05	0.112	3.3
Azarshahr	10.95	3.02	0.106	3.3
Oskou	11.17	3.11	0.108	3.5
Malekan	10.76	3.03	0.112	3.4
Ahar	10.85	3.06	0.114	3.5

DM-Dry Matter TPN- Total Protein Nitrogen NPN-Non Protein Nitrogen

Mean concentrations of cadmium and lead in cow's milk samples from East Azarbayjan are presented in Table2. The highest concentration of cadmium was found in the Sarab city $(4.52\pm0.82 \text{ pbb})$ and the lowest ones in the Malekan city $(0.57\pm0.15 \text{ pbb})$. The highest concentration of Lead was found in the Meyaneh city $(182.08\pm20.25 \text{ pbb})$ and the lowest ones in the Ahar city $(12.82\pm1.91 \text{ pbb})$. Statistical analyses showed that there are significant differences between lead and cadmium concentrations in raw cow's milk samples from different regions of East Azarbayjan province. In all the samples measured cadmium contents, was less than authorized limit by FAO/WHO

^[5] standard (Cd: $10\mu g/kg$). But only in 28% the samples measured Lead contents, was less than authorized limit by FAO/WHO standard (Pb: $20\mu g/kg$). The levels of metals in cow's milk are show in Table 2.

Treatment Samples Number	Pb	Cd	
Treatment	Samples Number	mean±SD	mean±SD
Meyaneh	10	$182.08^{a} \pm 20.25$	$1.07^{d} \pm 0.30$
Malekan	8	142.16 ^b ±4.34	$0.57^{d} \pm 0.15$
Oskou	10	134.75 ^c ±8.94	$3.89^{ab} \pm 0.79$
Sarab	10	$65.45^{d} \pm 3.72$	$4.52^{a}\pm0.82$
Azarshahr	20	$65.42^{d} \pm 9.11$	$3.01^{bc} \pm 0.62$
Maragheh	14	$28.38^{e} \pm 4.34$	$1.46^{d} \pm 0.43$
Tabriz	20	$13.99^{f} \pm 2.81$	$1.21^{d}\pm0.50$
Ahar	8	$12.82^{f} \pm 1.91$	$2.60^{\circ} \pm 0.62$

Table2- Mean concentration of Lead and Cadmium in milk samples (ppb)

The content of mineral components and trace elements in milk is determined by a variety of factors, including mainly the content of a given element in soil, the content of energy in feed, the level of such organic components as fats, vitamins, protein, changes in absorption and retention of a given element [7]. Transhumance along roads and/or motorways, fodder contamination, climatic factors, such as winds, and the use of pesticide compounds [4]. Important factors that influence the occurrence of many trace elements, including toxic ones, are environmental pollution, mainly of anthropogenic origin [20]; as well as phenomena of inter element interactions [8]. Therefore, in the literature available different data are reported. Flynn reports the following elemental composition of milk: I – 0.1 – 0.77 B – 0.5 – 1.0, Fe – 0.5, Si – 3.0, Zn – 3.5 mg/l and Cr –2.0, Sc – 10, F – 20, Ni – 26, Mn – 30, As – 20 – 60, Mo – 50 and Cu – 90 μ g/l [6].

Licata *et al.*, 2004[11] analyzed milk samples of 40 cows in Calabria, Italy. The highest lead concentrations amounted to 9.92 μ g/kg. The cadmium levels were below the detection limit of 0.01 μ g/kg in almost all the samples. Only in three milk samples were the cadmium concentrations higher: 1.14, 3.42 and 22.8 μ g/kg. Our data regarding the concentration of Cadmium and Lead were higher than that report.

Rodriguez *et al.*, 1999[19] determined the heavy metals in samples of raw cow's milk in Spain. The concentration of cadmium accounted for 4.88 μ g/L (0.7–23.1 μ g/L), whereas that of lead for 14.82 μ g/L (1.3–39.1 μ g/L). The concentration of Cadmium (but in the concentration of Lead) the present study was lower than those reported earliest studies. National monitoring studies in Poland reported mean concentration of lead at 3 and that of cadmium at <1 mg/kg in 2000[17] and similar levels in 2001 [18]. Our results are similar or lower than those reported from other countries currently.

CONCLUSION

In all the samples measured cadmium contents, was less than authorized limit by FAO/WHO standard. But only in 28% the samples measured Lead contents, was less than authorized limit by FAO/WHO standard. The location of cows has a significant impact on the content of many microelements and trace elements in milk. Lead and Cadmium causes dangerous effects on human organs, and we should do our best to decrease the amount of the abovementioned metals. Further studies are necessary to evaluate the contents of toxic heavy metals on a greater number of milk samples from various producers in Iran and to confirm the absence of possible toxicological risks.

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