Journal of Microbiology,
Biotechnology and
Food Sciences

Lukáčová et al. 2012 : 2 (2) 795-802

REGULAR ARTICLE

CONCENTRATION OF SELECTED ELEMENTS IN RAW AND ULTRA HEAT TREATED COW MILK

Lukáčová Anetta[1], Massányi Peter [2], Greń Agnieszka [3], Golian Jozef [1]*

Address: [1]Slovak University of Agriculture, Faculty of Biotechnology and Food Sciences, Department of Food Hygiene and Safety, Tr. A. Hlinku 2, 949 76 Nitra, Slovak Republic
[2]Slovak University of Agriculture, Faculty of Biotechnology and Food Sciences, Department of Animal Physiology, Tr. A. Hlinku 2, 949 76 Nitra, Slovak Republic
[3]Pedagogical University, Department of Animal Physiology and Toxicology, ul. Podbrzezie 3, 31-054 Kraków, Poland

* Corresponding author: anetta.lukacova@uniag.sk

ABSTRACT

The potential presence of toxic metals in food is being recognized as a priority by standards organizations and constitutes an analytical challenge. The toxic metal content of milk and dairy products is due to several factors: environmental conditions, the manufacturing process and the possible contamination during several steps of the manufacturing processes. The aim of this study was to evaluate samples of raw milk with fat contents 3.8% obtained at randomly from animal farms in around Nitra, western Slovakia region and ultra – heat treated cow milk (UHT) with fat contents 1.5% commercially available from local market in Nitra. Samples of milk were analysed for metal contents using atomic absorption spectrophotometry (AAS). UHT milk showed higher levels of cadmium, nickel and iron. Higher levels of zinc, copper were detected in raw milk. Significant differences in the concentration of copper between raw and UHT cow milk were found.

Keywords: metals, raw milk, ultra – heat treated cow milk

INTRODUCTION

Milk is considered as a nearly complete food since it is a good source for protein, fat and major minerals **(Enb et al., 2009)**. Milk is an important source of all basic nutrients required for mammals including human beings. Milk from various mammals such as cow, buffalo, goat, sheep is used for different nutritional purposes, e.g. feeding to young ones and preparation of some nutritional products such as milk cream, butter, yogurt, sour milk, etc. **(Hassan, 2005).**

The major chemical components of milk include water, fats, proteins, carbohydrates, minerals, organic acids, enzymes and vitamins **(Dobrzanski et. al, 2005).** Milk and milk products are the most diversified of the natural foodstuffs in terms of composition, contains more than twenty different trace elements **(Stawarz et al., 2007)**. Most of them are essential and very important such as copper, zinc, manganese and iron. These metals are cofactors in many enzymes and play an important role in many physiological functions of man and animals **(Koh and Judson, 1986).**

Increasing industrialization has been 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 **(Florea et al., 2006)**. Contamination of food products by heavy metals is becoming an unavoidable problem. These agents have led to metal dispersion in the environment and consequently, impaired health of the population by the ingestion of victuals contaminated by harmful elements **(Žukowska et al., 2008)**.

The amount of metals in uncontaminated milk is admittedly minute, but their contents may be significantly altered through manufacturing and packaging process as well as metals that may contaminate feed and environment such as cadmium, chromium, nickel and cobalt could be excreted into milk at various levels and causing serious problems **(Schuhmacher et al., 1991)**.

Toxicity of metal is closely related to age, sex, route of exposure, level of intake, solubility, metal oxidation state, retention percentage, duration of exposure, frequency of intake, absorption rate and mechanisms/efficiency of excretion **(Mertz, 1986)**.

Those metals described as "heavy metals" which, in their standard state, have a specific gravity of more than about 5 $g.cm^{-3}$. Some of them, such as cooper, nickel, manganese, chromium and iron are essential in very low concentration for the survival of all forms of life **(Watson, 2001)**.

Only when they are presented in higher quantities, can these, like the heavy metals lead, cadmium be toxic also in very low concentrations and cause metabolic anomalies **(Hernandez-Avila et al., 2003)**. Here, the boundary between the essential and toxic effects is somewhat problematic **(Thomas, 2006)**.

According to the Order of the Ministry of Agriculture of Romania, the maximal admitted for contaminating heavy metals in milk and cheese, are: 0.05 mg/kg for cadmium and 0.05 for mercury (the cadmium and the mercury are indexed only in case of meat and of marine animals meant for human consumption) **(Florea et al., 2006)**

The aim of this study was to evaluate concentrations of selected metals in raw and ultra – heat treated cow milk and based on the results to determine the dependence between analyzed metals.

MATERIAL AND METHODS

Materials

Samples (n=30) of raw and ultra – heat treated cow milk (UHT) were collected. The samples of raw milk with fat contents 3.8% were obtained random by from animal farms in region Nitra, western Slovakia. The samples of UHT cow milk with fat contents 1.5% commercially available were purchased from local market in Nitra. The samples were collected during the period from 2011 to 2012.

Methods of Analysis

Analysis involved the digestion of 1 g of samples with 20 mL of Analar grade $HClO_4$ and HNO_3 in proportion 4:1 which was be carried using validate methods of analysis. Samples were mixed at temperature of 120°C for about 65 min, cooled and transferred into 25 mL standard flask and filled to the final volume with deionised water. The content of the following elements (cadmium, zinc, nickel, iron and copper) were measured with voltammetric method **(Stawarz et al. 2007)**.

Metals were extracted from the milk according to AOAC method. The metals were measured by atomic absorption spectrophotometry (AAS). Maximum absorbance was obtained by adjusting the cathode lamp at specific slit and wave lengths. Fe was measured at 248.3 nm, Cu at 324.8 nm, Zn at 319.9 nm, Cd at 228.8 nm, Ni at 232.0 nm. The obtained results were expressed in $mg.kg^{-1}$.

Statistical analysis

Basic variation statistical values (arithmetic mean, standard deviation, coefficient of variation, maximum and minimum value) were calculated. The significant differences between means were calculated by a one-way analysis of variance using Duncan´s multiple-range test at $P<0.05$ and correlation assay.

RESULTS

Result of element concentration in raw milk samples collected from animal farms in Nitra region and UHT milk are shown Table 1. Higher cadmium concentration in UHT milk 0.33 ± 0.24 $mg.kg^{-1}$ in comparison the raw milk 0.27 ± 0.19 $mg.kg^{-1}$ was determined. The cadmium concentration was in the interval from 0.10 $mg.kg^{-1}$ to 0.73 $mg.kg^{-1}$ in raw milk and 0.21 $mg.kg^{-1}$ – 0.94 $mg.kg^{-1}$ in UHT milk.

Zinc and copper was found at highest levels in raw milk (13.09 and 3.90 $mg.kg^{-1}$, respectively). Significant differences at the significance level $P<0.01$ in the concentration of copper between raw and UHT cow milk were found. Concentration of nickel was in the range from 0.53 to 1.37 $mg.kg^{-1}$ with an average value 1.01± 0.32 $mg.kg^{-1}$ in the UHT milk and with average value of nickel 0.84 ± 0.42 $mg.kg^{-1}$ in the raw milk.

Table 1 Basic variation statistical characteristics of the average content of elements

	Elements									
	Cd		Zn		Ni		Cu		Fe	
	R	UHT	R	UHT	R	UHT	R	UHT	R	UHT
mean	0.27	0.33	13.09	11.39	0.84	1.01	3.90	0.95^{B}	1.76	1.92
median	0.21	0.26	12.12	11.35	0.81	1.09	1.90	0.92	1.56	1.81
SD	0.19	0.24	4.49	1.97	0.42	0.32	0.41	0.25	1.13	1.45
CV	70.69	73.36	34.28	17.31	50.58	32.09	104.62	26.00	64.29	75.77
MIN	0.10	0.21	6.97	8.35	0.25	0.53	0.64	0.64	0.0	0.55
MAX	0.73	0.94	23.88	14.96	1.65	1.37	11.89	1.2	4.09	2.57

Legend: SD – standard deviation, CV (%) – coefficient of variation, MIN – minimum value, MAX – maximum value, R – raw milk, UHT - ultra – heat treated cow milk; ^{B} P<0.01

The average concentration of iron was higher in UHT cow milk (1.92 ± 1.45 mg.kg^{-1}) than in raw milk (1.76 ± 1.13 mg.kg^{-1}). The content of iron was in the range from 0.55 mg.kg^{-1} to 2.57 mg.kg^{-1} in the UHT cow milk and from 0.00 mg.kg^{-1} to 4.09 mg.kg^{-1} in the raw milk.

Figure 1 Average concentration of elements in raw and UHT cow milk

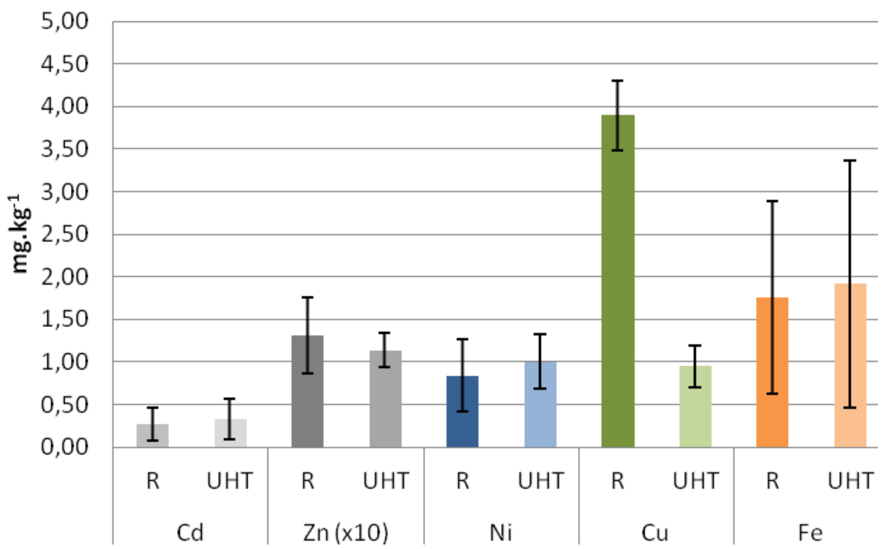

Table 2 Correlations observed in the concentration of metals in different types of milk

	Cd/R	Cd/UHT
Cu/R	r = 0.767 p = 0.01	
Cu/UHT		r = 0.602 p = 0.066
Zn/UHT		r = 0.618 p = 0.057

Legend: R – raw milk, UHT - ultra – heat treatment processed cow milk, p, r - correlation coefficients

The high positive correlation was detected between the Cd and Cu in raw cow milk (r = 0.767; p=0.01). Medium positive correlation was found between Cd and Cu; Cd and Zn, in ultra- heat treated cow milk (r = 0.602, r = 0.618, respectively).

DISCUSSION

Cadmium is the important inorganic contaminant entering into the food chain from the environment. Burning of fossil fuels, coal productions and application of some phosphate fertilizers are sources of contamination **(Žukowska and Biziuk, 2008)**. Mean concentration of cadmium in raw and UHT milk (0.27 and 0.33 $mg.kg^{-1}$, respectively) were compared with mean levels of cadmium in raw milk samples of **Abou-Arab et al (1997)** which were collected from Cairo during the period 1990 – 1992 and **Koops et al. (1988)**. The authors reported that Cd was 0.348 $mg.kg^{-1}$ and 0.356 $mg.kg^{-1}$. This value of raw milk was higher than presented in this study. The Codex Alimentarius of the Slovak Republic determines the maximum levels of cadmium 0.01 $mg.kg^{-1}$ in food products for nutrition of children. Our results show that these values are exceeded in raw and UHT milk.

The mean Zn concentration in raw milk was 13.09 $mg.kg^{-1}$ and the Zn concentration in the commercial cow milk samples was 11.39 $mg.kg^{-1}$. These concentrations were higher than those determined in **Enb et al. (2009)**.

Enb et. al (2009) reported level of copper in milk from buffalo and cow (0.212 $mg.kg^{-1}$ – 0.142 $mg.kg^{-1}$, respectively). In our measurement we detected the value of copper in raw milk and UHT milk (3.90 $mg.kg^{-1}$ – 0.95 $mg.kg^{-1}$, respectively).

The concentration of iron in raw milk (1.76 $mg.kg^{-}1$) observed in this study is higher than those observed in fresh cow milk (0.72 $mg.kg^{-1}$) in study of **Birghila et al. (2008)**. But, the concentration of iron in commercial milk samples observed in this study were lower than those observed in commercial milk samples from **Kondyli et al. (2007)**.

Nickel has been analyzed in food and fodder since 1990. **Enb et al. (2009)** compared the concentration of nickel in cow (0.004 $mg.kg^{-1}$) and buffalo milk (0.006 $mg.kg^{-1}$). Our results revealed that, levels of nickel under study were higher than levels **Enb et al. (2009)**.

The purpose of this study was to focus concentration of selected metals in raw and ultra – heat treated cow milk. The results of this study showed higher concentration of copper and zinc in raw milk than by UHT milk and a higher concentration of cadmium, nickel, iron in ultra – heat treated cow milk in comparison raw milk was determined. Based on the analysis we observed higher metal concentration (cadmium, nickel and copper) in raw milk and UHT milk which were compared with food standards.

Acknowledgement: This work was supported by the Ministry of Education grants VEGA (grant number 1/0532/11) and KEGA (grant number 013SPU-4/2012).

REFERENCES

ABOU-ARAB, A.A.K. 1997. Effect of Ras cheese manufacturing on the stability of DDT and its metabolites. In *Journal Food Chemistry,* vol. 59, 1997, no. 1, p. 115-119.

AOAC, Association of Official Analytical Chemists 1997. *Official Methods of Analysis*, Maryland, 128-145.

DOBRZANSKI, Z. - KOLACZ, R. - GÓRECKA, H. - CHOJNACKA, K. - BARTOWIAK, A. 2005. The content of microelements and trace elements in raw milk from cows in the Silesian region. In *Polish Journal Environmental Studies,* vol. 14, 2005, no. 5, p. 685 – 689.

ENB, A. - ABOU DONIA, M.A. - ABD-RABOU, N.S. - ABOU ARAB, A.A.K. - EL SENAITY, M.H. 2009. Chemical composition of raw milk and heavy metals behavior during processing of milk products. In *Global Veterinaria*, vol. 3, 2009, no. 3, p. 268-275.

FLOREA, T. - ORBAN HUSZTI, S. - COSTIN, M.G. 2006. Heavy metal contaminants in milk and cheese. In *The Annals of the University Dunarea de Jos of Galati*, *Fascicle VI – Food Technology*, 2006, p. 26-32

HASSA, I.P. 2005. Quality Assurance of Various Dairy Products. MSc Thesis, Department of Chemistry, University of Peshawar, Pakistan: 86-89

HERNANDEZ-AVILA, M. - GONZALEZ-COSSIO, T. - PETERSON, K.E. - PALAZUELOS, E. - HU, H. 2003. Dietary calcium supplements to lower blood lead levels in lactating women: a randomized placebo controlled trial. In *Epidemiology,* vol. 14, 2003, no. 2, p. 206-212.

KOH, T.S. - JUDSON G.T. 1986. Trace elements in sheep grazing near a lead-zinc smelting complex at Port Pirie South Australia. In *Bulletin of Environmental Contamination and Toxicology,* vol. 37, 1986, p. 87-95.

KONDYLI E. - KATSIARI M.C. - VOUTSINA L.P. 2007. Variations of vitamin and mineral contents in raw milk if the indigenous Greek breed during lactation. In *Food Chemistry,* vol. 100, 2007, p. 226-230.

KOOPS, J. - KLOMP, H. - WESTERBEEK, D. 1988. The cadmium an lead contents of Dutch milk. In *Netherlands Milk and Dairy Journal,* vol. 42, 1988, p. 99.

MERTZ, W.ED. 1986. Trace elements in human and animal nutrition, vol. I and II, 5 th ed., *Academic Press,* New York, 110-118

BIRGHILA, S. – DOBRINAS, S. – STANCIU, G. - SOCEANU A. 2008.determination of major and minor elements in milk through ICP-AES. In *Environmental Engineering and Management Journal*, vol. 7, 2008, p. 805-808.

SCHUHMACHER, M. - BORQUES, A.M. – DOMINGO, L.J. - CARBELLA, J. 1991. Dietary intake of lead and cadmium from foods in Tarragona Province, Spain. In *Bulletin of Environmental Contamination and Toxicology,* vol. 46, 1991, p. 320-328.

STAWARZ, R**.** – FORMICKI, G**.** – MASSÁNYI, P. 2007. Daily fluctuations and distribution of xenobiotics, nutritional and biogenic elements in human milk in Southern Poland. N *Journal Environ Science Health A Toxicology Hazard Substances and Environmental* Engineering, vol. 42, 2007, n. 8, p.1169-75.

STAWARZ, R. – MASSÁNYI, P. – FORMICKI, G. – LUKÁČ, N. – ZAKRZEWSKI, M. 2007. Xenobiotics, nutritional and biogenic elemens content in human milk in Poland in relation to age breastfeeding women In *Progress in environmental science and technology.* (Vol. I). -- S. 200-207. -- Beijing : Science Press, 2007. -- 978-7-03-020403-5.

THOMAS, D. 2006., Meat and dairy minerals. In *Food Magazine,* vol. 72, 2006, p. 10-15.

VÝNOS MP SR a MZ SR z 11. septembra 2006 č.18558/2006-SL.

WATSON, D.H. 2001. *Food chemical Safety* Watson D.H. (Ed), CRC Press Boca Raton FL, vol. 1, 1-12.

ŽUKOWSKA, J. - BIZIUK, M. 2008. Methodological evaluation of method for dietary heavy metal intake. In *Journal of Food Science*, vol. 73, 2008, no. 2, p. 21-29.