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**Abstract**. The aim of this research was to evaluate the possible contamination by heavy metals of milk from cows in Macedonia. The concentrations of heavy metals were determined in cow milk from the different farms, at three city (Kumanovo, Tetovo, Gotivar) in Macedonia. Each sample, homogenized and powdered, was mineralized in a microwave oven.
Quantitative analyses of Cd, Cr, Cu and Pb were performed using an atomic absorption spectrophotometer with graphite furnace. As was analyzed by hot vapor generation technique and Zn with the flame method.
The concentration of many metals is low (<0.1 mg/kg) such as: As,Co, Cd, Cr, Cu,Fe, Pb, and Zn.

**Key words**: chemical elements, milk, Macedonia.

## INTRODUCTION

Heavy metals are persistent contaminants in the environment that can cause serious environmental and health hazards. They are released into the environment from natural as well as man-made activities.
Some heavy metals (like Cu and Fe) are essential to maintain proper metabolic activity in living organisms; others (like Pb and Cd) are non-essential and have no biological role (Ayar et al., 2009; Qin et al., 2009). However, at high concentrations, they can cause toxicity to living organisms (Li et al, 2005).
Milk is known as an excellent source of Ca, and it can supply moderate amounts of Mg, smaller quantity of Zn and very small contents of Fe and Cu (Pennigton et al., 1995). On the other hand, due to the growing environmental pollution it is also necessary to determine and monitor the levels of toxic metals (TMs) in milk, because they can significantly influence the human health (Steijns, 2001; Licata et al., 2004)
The main objective of this study is to assess the concentration of mineral and trace elements in cow milk used for production of traditional dairy products, collected from three city in Macedonia.

## MATERIAL AND METHODS

Raw milk samples of cows were collected from a cow farm during the morning milking directly into sterile screw-topped bottles (500 ml), to avoid potential contamination due to metallic containers and collected tanks ( n = 60). Three milk samples were collected from three city in Macedonia.

**Sample analyses** each sample, homogenized and powdered, was mineralized in a microwave oven. Quantitative analyses of **Cd, Cr, Cu** and **Pb** were performed using an atomic absorption spectrophotometer with graphite furnace. As was analyzed by hot vapor generation technique and **Zn** with the flame method.

The concentration of many metals is low(<0.1 mg/kg) such as: As,Co, **Cd, Cr, Cu,Fe, Pb,** and **Zn.**

## RESULTS AND DISCUSSION

Metal concentrations (20 elements) in milk from three city (Kumanovo, Tetovo and Gostivar) are summarized in Table 1.

Cuprum (Cu) concentration tabulated in Table (1) was ranged from 2.15(Tetovo) to 2.76 mg/L(Kumanovo),while in Gostivar determined 2.42 mg/L.

Regarding to results in Table (1) the concentration of As, Cd, Co, Cr and Pb, in examined milk samples was low (< 0.1 mg/L), at all city. These result is nearly similar to those reported by **Cabrera et al.** (**1995**).

The concentration of Al in the milk is variable, with highest measured concentration observed in the milk samples collected from the Gostivar city (1,24 mg/ L ), while in Kumanovo and Tetovo it was lower(1 mg/L in Kumanovo, 0.72 mg/L, in Tetovo).

Concerning the concentration of K in the milk is also variable, with highest measured concentration observed in the milk samples collected from the Kumanovo city (1174 mg/ L ), while in Gostivar registered 724 mg/L, and Tetovo it was lower 595 mg/L in Kumanovo.

The results of Cu, show that in Kumanovo is registered the higher concentration (2.76), compared with Tetovo and Gostivar.

**Table 1**. Determination of Chemical elements at milk , at three city in Macedonia(Kumanovo, Tetovo, Gostivar)

| | Chemical elements | Kumanovo Milk mg/L | Tetovo milk mg/L | Gostivar Milk mg/L |
|---|---|---|---|---|
| 1 | Al, mg/L | 1.00 | 0.72 | 1.24 |
| 2 | As, mg/L | <0.1 | <0.1 | <0.1 |
| 3 | B, mg/L | 0.56 | 0.35 | 0.69 |
| 4 | Ba, mg/L | 0.25 | 0.10 | 0.14 |
| 5 | Ca, mg/L | 1122 | 697 | 947 |
| 6 | Cd, mg/L | <0.1 | <0.1 | <0.1 |
| 7 | Co, mg/L | <0.1 | <0.1 | <0.1 |
| 8 | Cr, mg/L | <0.1 | <0.1 | <0.1 |
| 9 | Cu, mg/L | 2.76 | 2.15 | 2.42 |
| 10 | Fe, mg/L | 3.82 | 2.08 | 1.74 |
| 11 | K, mg/L | 1174 | 595 | 724 |
| 12 | Mg, mg/L | 80.8 | 74.8 | 71.0 |
| 13 | Mn, mg/L | 0.039 | 0.028 | 0.025 |
| 14 | Na, mg/L | 255 | 489 | 235 |
| 15 | Ni, mg/L | <0.1 | <0.1 | <0.1 |
| 16 | P, mg/L | 786 | 504 | 634 |
| 17 | Pb, mg/L | <0.1 | <0.1 | <0.1 |
| 18 | Sr, mg/L | 0.95 | 0.32 | 0.63 |
| 19 | V, mg/L | <0.1 | <0.1 | <0.1 |
| 20 | Zn, mg/L | 3.17 | 2.27 | 3.28 |

The term Heavy Metals refer to any metallic element that has a relatively high density and is toxic or poisonous at low concentration (**Lenntech**, 2004). Heavy Metals are a general collective term, which applies to the group of metals and metalloids with atomic density greater than 4 g/cm3 , or 5 times or more, greater than water (**Symon and Huton,1986; Nriagu,1988; Hawks,19**97) and also Heavy Metals are defined as those elements with a specific density at least five times the specific gravity of water, Heavy Metals include Cadmium (Cd), Copper (Cu), Lead (Pb), Zinc (Zn), Mercury (Hg), Arsenic (As), Silver (Ag), Chromium (Cr), Iron (Fe) and Platinum group elements, Copper and Zinc are essential trace elements for living organisms at low concentration (10mg/L).

Heavy metals are elements such as Cu (Copper), Cd (Cadmium), Ni (Nickel), Pb (Lead), Zn (zinc), Ag (Silver), Cr (Chromium), Hg (Mercury), Fe (Iron), Co (Cobalt) and As (Arsenic) which are usually associated with toxicity and are natural components of the earth's crust. They cannot be degraded or destroyed. To a small extent they enter our bodies via food, drinking water and air. As trace elements, some heavy metals (e.g. Copper, Selenium, and Zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking water contamination (e.g. through Lead pipes), high ambient air concentrations near emission sources, or intake via the food chain.

From the nutritional point of view, metals contents of milk and dairy products can be grouped into essential elements (iron, copper and zinc) at low doses and non essential or toxic ones (lead and cadmium). The presence of the latter, even in low concentrations, is invaluable and leads to metabolic disorders with extremely serious consequences ( Khan, 2008).

Zinc concentrations in milk samples were in the ranges of 2.27(Tetovo)–3.28 (Gostivar), while in Kumanovo registred 3.17 mg/L.

These values are similar with the levels obtained by Malhat et al. (2012) and those reported by Simsek et al. (2000).
Zn is indispensable for the structure and the activity of more than 300 enzymes responsible for nucleic acid and protein synthesis, cellular differentiation and replication, insulin secretion, sexual maturation and it may also be involved in the functional performance of the immune system and other physiological processes (Vahcic, 2010).
The values of Cu either in kareish cheese or in milk were closely related to values reported by Dobrzanski et al. (2005).
Copper as an essential trace element is necessary for the adequate growth, integrity of the cardiovascular system, elasticity of the lungs, neuronendocrine function, and iron metabolism (Sieber 2006).
The values of iron in milk are much higher than the values reported by Simsek et al. (2000).
Iron as an essential trace element participates as catalyst in several metabolic reactions. As a component of hemoglobin, myoglobin, cytochromes and other proteins, plays an essential role in the transport, storage and utilization of oxygen. It is also a cofactor for a number of enzymes and its deficiency results in anemia. The daily intake (mg/day) for Fe in the milk and dairy products ranged from 0.04 to 1.799 mg/day.

## CONCLUSION

According to obtained results we can conclude , that all samples of milk contain heavy metals , under the permissible limits.

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