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Heavy Metals in the raw Milk in Mitrovica

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Abstract

Safe and quality of food are of primary importance for food industry. The aim of this study was to measure the heavy metals concentration in the raw milk in Mitrovica, a region with a rapid industrial development. Trepca complex, for example is one of the key sources of heavy metal contamination of the region. The purpose of this paper, initially, was to understand the role of food contaminants that until recently were considered as antidote for heavy metals. Samples were prepared in the oven combustion and the remained calyx was treated with nitric acid. Samples were analysed at the atomic absorber and the concentrations of three heavy metals in milk were measured. The results demonstrate that the milk from this area was contaminated with Pb and the highest concentration of this heavy metal was detected during the summer (L_V = 2,048 mg/l). The concentration of Zn, one of the essential metals in milk, was reduced to Z_D = 0.1506mg/l during winter time. The concentration of Cd, a toxic heavy metal, resulted to be high in all areas, reaching the highest level (B_V= 0.1152) in summer.

Keywords: milk, heavy metal, toxicity

Introduction

Milk, as very important food product, is essential in our kitchen. Based on the sensitivity of the gastrointestinal tract of infants and generally to all organisms, chemical and microbiological composition of milk is very important. This chemical composition is influenced by the food consumed by animals and the environment surrounding them. Microelements reach milk as they get into the food chain of animals through the environment. Heavy metals as arsenic (As), cadmium (Cd), mercury (Hg) and lead (Pb) have no beneficial effect on people. [9]

Crops irrigated with discharged waters consumed by cows and buffaloes as foods have a high presence of lead and cadmium in contrast to crops irrigated by irrigation's system. [1]

In most cases, chemical residues and contaminants are resistant to dissolution and thermal treatment, such as pasteurization or increase of the pH during fermentation, will have the no effect of.[12]

Heavy metal ions denaturalize proteins by attacking group-SH. Egg and milk proteins denaturalizes by metal ions by creating insoluble precipitation of in the stomach, which should be extracted from the body by inciting the vomiting. If antidotes are not extracted from stomach, digestive tract enzymes dissolve protein releasing toxic ions of heavy metals. [2]

Lead-lead intoxication in humans in known since from the second century BC. Cardiovascular, hematological and neurological problems occur even in exposures to low quantities, problems in urinary, digestive, hepatic and immune system occur when exposed to higher levels. [7]

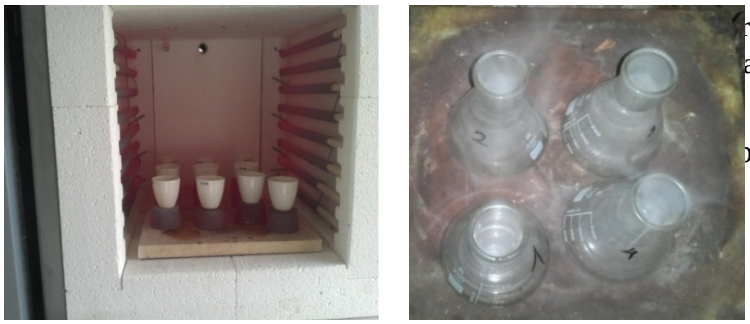
Zinc - Zinc is an essential trace element, necessary for the functioning of several enzyme's systems, but excessive quantities of zinc coming from geological sources adversely affectswater and food quality. Zinc toxicity symptoms include vomiting, dehydration, abdominal pain, nausea, lethargy, dizziness and muscle's incoordination. Depending on age and sex, daily zinc requirements are between 3.2 and 29 mg for different countries.[10]

Cadmium-Cadmium is more known by its toxicity and metabolic antagonism with Zn and other elements. Contamination of pastures with Cd can increase the content in grasses for about 40 times. Some plants (eg. oat) have the ability to concentrate cadmium received from soil.[11]

According to *A. Zaidi, PA Wani* [15], inflammation symptoms may occur several hours after exposure and include cough, dehydration, nose and throat irritation, headache, dizziness, weakening, chest pain.

Materials and methods

Sampling was conducted in two periods, in a summer and winter. Samples were taken from cow's milk, mixed of morning and evening milking. Sampling was conducted in the vicinity of Mitrovica, by 5 samples for each sampling point. Sampling was conducted in: Lower Zhabar, Bare, Frasherand LowerLisica villages



(a) (b)

Figure 1. Samples treatment: a) combustion in a furnace), b) treatment with nitric acid

Preparation of milk samples for SAA analyses

Five (5) ml from each milk sample was placed in different crucibles and heated in a maple furnace at a temperature of 700^{O}C for 3 hoursas shown in **Figure.1a)** to vaporize all other components and leave the tailings of heavy metals as a pure calyx.

The calyx was cooled to room temperature before being dissolved in a 5 ml solution ofnitric acid (1:6) to compound with the heavy metal, if present. The solution was subsequently heated and evaporated to half of its volume using a hot plate as in **Figure1.b).** The resulting solution was then poured into a volumetric flask, rlenmeyer flask, and topped up to 25ml with distilled ater.[5]

Samples were then analysed with atomic sorption spectrophotometry. [13]

Results and discussion

Results will be presented for each element as the average results of five samples for each sampling location in two seasons of the year.

Based on Regulation (EC) Nr. 1881/2006, of 19 December 2006 pursuant to Annex B, for "Raw milk (6), heat-treated milk and milk for the manufacture of milk-based products" limiting the maximum level of 0.020mg /l, [3], from the Table 1. understand that seven out of eight samples have exceeded the maximum limit

Table 1. Presentation of the results of Lead concentration in summer and winter season in four locations

Pb mg/l	Zhabar	Frashër	Lisicë	Bare
Winter	0.3088	1.1114	1.422	0.2042
Summer	0.2524	0.272	2.048	0.008

Lead as heavy metal, compared with cadmium is more concentrated, while the milk in Lisica village is the most contaminated, which is closer to the source of contamination, contamination is higher during the summer season LV = 2.048mg / l and this due water from Sitnica river that cattle have used for drinking which contains contaminates from power plant and Trepca flotation discharging.

Milk that has shown satisfactory concentration of lead are milk samples from Bajgora area, more precisely the village Bare, where the average concentration in a summer season is below the maximum limit BV = 0.008mg / l. In general the results are alarming, as industrial wastes have reached wider radius from the source of contamination.

As per recommendations of WHO [14] the presence of zinc in raw milk should be at the level of 3-5 mg/l.Some of the authors [8], also recommend that zinc concentrations should range between 2-6 mg/l. From Table 2,we can see that in all samples the average concentration is below the limited level,and milk can be considered as deficient regarding this essential element, but the problem lies when this milk is used for infants, to whom represents the only source of Zn ions. These low levels are directly associated with animal feeding rations which especially during the winter season have been poor with nutrition elements. A slight increase of the level of Zn ions observed in summer season when during the cattle grazing on pasture.

Table 2. Presentation of the results of Zinc concentration in summer and winter season in four locations**.**

Zn mg/l	Zhabar	Frashër	Lisicë	Bare
Winter	0.1506	0.212	0.35	0.176
Summer	**0.342**	**0.422**	**0.55**	**0.442**

Table3. Presentation of the results of Cadmium concentration in summer and winter season in four locations.

Cd mg/l	Zhabar	Frashër	Lisicë	Bare
Winter	0.01	0.001	0.0052	0.0298
Summer	**0.0304**	**0.0466**	**0.0236**	**0.1152**

Based on the reports for scientific cooperation between European Union member states[6], Provisional Tolerable Weekly Intake (PTWI) of cadmium is determined at 0.007mg/kg (mg/l) per body weight.And, based on the publication of the Council of Europe [4], for milk and milk products in Germany limitation presence of cadmium is 0.005mg/l. Comparing with these limitations, six out of eight samples analysed in this paper, have exceeded the maximum allowed limits. Based on previous levels and based on the well-known toxic effects of cadmium, detected results are disturbing

as only two of these samples are in the average of allowed levels.

Conclusions

Based on the experimental results obtained in this paper, we can bring the following conclusions:

Raw milk, based on the results obtained from tests, appears to be greatly affected by concentration of two the toxic heavy metals, having very high values in two locations that are geographically very close to the source of contamination. These two areas that are severely affected are: the area around the Frashër village and surrounding area of Lisica village.

Two villages are, in principle, considered less affected. However, even these areas are substantially affected by contamination with heavy metals as a consequence of atmospheric conditions. In the area of village Zhabar, concentration of two toxic metals values are of concern about the fact that shows resistance of this type of contamination and high range of contamination's transfer effect. The most disturbing fact is that concentrations above the permitted values are also in the area of the village Bare, having cadmium with the higher concentration above the maximum limits, known for toxicity and as a substance of carcinogenic reaction when inside the human body. The sources of these metals may also be as a consequence of the agricultural activity as are pesticides, which becomes doubtful when the same sample shows high concentration of Cd in both seasons and significantly differs from the other four samples.

Based on the results obtained from the tests, we can conclude that the essential metal Zn we have tested, concentrations are insufficient and this is reflected in all areas with insignificant differences between seasons, with a little increase to values in summer period.

A risk is related to all three metals: two toxic metals are above the maximum levels and for sensitive category of consumers effects are alarming, causing growth developmental delay or having carcinogenic effect. The other problem is deficiency of essential metal Zn. As milk is known as the source of all minerals and nutritional values with particular emphasis for new-born babies, then we conclude that consumption of only this milk for infants will cause deficiency of this essential microelement to organism. This will lead to disorders which can easily return to irreversible disorders as is Dwarfism.

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