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HEAVY METALS CONTENT IN SHEEP PRODUCTS FROM MIDLE SPIŠ

Slávik Marek[*1], *Tóth Tomáš*[2], *Kopernická Miriama, Árvay Július, Harangozo Ľuboš*

Address(es): Ing. Marek Slávik
[1]Slovak University of Agriculture, Faculty of Biotechnology and Food Science, Department of Chemistry, Tr. A. Hlinku 2, 949 76 Nitra, Slovakia, phone number: +421 37 641 4376.
[2]Slovak University of Agriculture, Faculty of Biotechnology and Food Science, Department of Chemistry, Tr. A. Hlinku 2, 949 76 Nitra, Slovakia.

*Corresponding author: marekslavik87@gmail.com

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ABSTRACT

In this work, we evaluated the risk of contamination of animal products by heavy metals. Samples of animal raw materials were obtained in 2013 in the municipalities of Porac and Matejovce nad Hornádom. Samples of muscle and internal organs were collected from domestic sheep (*Ovis aries*) reared in the village of Rudnianska burdened area where mercury along with other heavy metals contamination is above the limit value of agricultural soil. Measuring the concentration of heavy metals in the samples was performed in accordance with the general requirements set out in the tenth chapter of the Food Code of the Slovak Republic. Mercury content in biological materials were assessed by total mercury as on the AMA 254 in fresh samples. The other heavy metal content, was determined after wet mineralization (HNO3: H2O - 1: 1) using the device AAS *Varian 240 FS*. The contamination of the environment showed increased accumulation of heavy metals in the - studiet sheep tissues intended for consumption. Such as Hg content in the kidneys of domestic sheep exceed the limit value by 1.3 times, whereas, in the case of cadmium 3 times exceeding the limit value in meat was recordered. Exceed limit was recorded in the case of lead and copper in the liver.

Keywords: Heavy metals, mercury, soil, food chains, sheep, animal products, safety of consupmtion

INTRODUCTION

According to a report on the status of the environment SR (2013) in terms of environmental quality is Rudňany area classified as a region with considerable disturbance, called Rudňany district. It has a slightly warm and humid climate. The relief area is slightly to moderately declining. The area has a rural character. At present the main sources of pollution are mining, engineering industries and metallurgy of non-ferrous metals. From the industrial enterprises in the region are mainly KOVOHUTY, as Krompachy. In terms of emissions of mercury, most important industrial source of pollution was the former plant Iron ore mines Spišská Nová Ves, np. Mining and ore processing takes place in the region since the 14th century, the intensive development occurred mainly in the late 19th century arose after 1895 in the village Rudňany Edit and ore roasters. Part of technologies were condensing towers of the mercury. The most intensive industrial production of mercury in the region took place from 1963 to 1993, when mentioned Iron ore mines Spišská Nová Ves np. emitted into the air from a plant in the village Markušovce, 120 tons of mercury (VÚG SAV). This constituted one of the greatest sources of mercury emissions in Europe at all (**Závodský, 1991**). Molecular basis of toxicity of heavy metals is a complex cascade of interrelated events that may directly or indirectly interfere with the pathological condition of specific organ systems (**Marcelo et al. 2005**). Basically, it's blocking the necessary functional groups in biomolecules and also extruding basic metal ions from them. Mercuric ion is known as one of the strongest thiol-linking intracellular agents. Therefore binds to the protein thiol residues particularly cysteine and glutathione. The result is a blocking inactivation of sulfur and related enzymes, cofactors, and hormones (**Zahir et al. 2005**). Soil is the most important template for the cycle of heavy metals in the food chain, and is naturally also indispensable for plant growth. Plants are an essential component of the food chain, whether directly consumed or used as fodder for livestock. They therefore represent a critical point of entry of heavy metals into the human diet. Long-serving deposition of soil to grow crops, or as permanent grassland, imissions of heavy metals leads to its deterioration and load (**Kabata - Penda 2001**). As already mentioned Rudnianska area has a rural character and there developed livestock especially sheep. The importance of keeping them is the provision wool meat and milk. In a region dominated by holdings in particular breeds cigája and Improved Valachian. Their meat, milk and dairy products are part of the food chain of the local population. Heavy metal contamination of the food items is one of the most important aspects of food quality (**Mohamed, 2012**).

AIM OF THE WORK

The aim of the work was to clarify the burden of animal products with heavy metals in polluted area.

MATERIAL AND METHODS

Study area

The content of heavy metals in soils in grassland areas of Rudnianska were characterized in Table 1. The area is heavily burdened with excessive values of heavy metals in agricultural soils.
Transfer factor (TF) = concentration of heavy metal in plant material / concentration of heavy metal in soil in which the plants were grown
Transfer factor from the soil in above-ground portions was defined as the ratio of the concentration of metal in the above-ground portions (in the fresh mass) to the total concentration of the metal in the soil (dry weight).

Collection of animal samples

All samples were collected in 2013.
From the village Matejovce nad Hornádom, we obtained specific muscle samples (n=2), kidney (n=2) and liver (n=2) of sheep (Ovis aries) at age 19 months (breed: Cigája) were obtained.
From the village Poráč samples were obtained from domestic sheep (Ovis aries) at age 19 months (breed: Cigája) samples of muscle (n=4), kidney (n=4) and liver (n=4). and non-smoked sheep cheese (n=3).

Analysis

Extraction of soil HNO_3 + HCl (1:3)) in terms of the current legislation (Law no. 220/2004 Coll on the conservation and use of agricultural land) was proceeded in accordance with the applicable methodology, and heavy metal content was determined by *Varian 240 FS*.
Extraction of plant and sheep products HNO_3 + H_2O (1:1) in terms of the current legislation (Law no. 220/2004 Coll on the conservation and use of agricultural land). Heavy metal content was determined by AAS method using *Varian 240 FS*.
To determine the content of total mercury in all samples, we used the same device. AMA 254 (Advanced Mercury Analyser)), which is special purpose atomic absorption spectrophotometer for the direct determination of mercury in

solid and liquid samples without the need for chemical pretreatment of the sample (mineralization etc.). Using the technique of generating a vapor of metallic mercury with subsequent interception and enrichment on a gold amalgamator achieves a high sensitivity setting and independence the result of determining the sample matrix. All mercury concentrations were expressed in mg. kg^{-1} fresh matter. [mg. kg^{-1} f.m.].

Determination of contaminants in meat, innternal organs and cheese were conducted according to the methodology set out in the Ministry of Agriculture of the Slovak Republic and the Slovak Ministry of Health of 25 November 2005, no. 3445/ 2005-100 establishing a chapter of the Food Codex of the Slovak Republic providing for methods of sampling and analysis for the official control testing for certain contaminants in foodstuffs. Statistical analysis were

RESULTS AND DISCUSSION

Heavy metals content in the analyzed samples of biological material and comparison with the limit value established by the Codex Alimentarius SR were shown in Table 2.

Table 1 contamination of pasture with heavy metals in Rudňany burdened area

Samples		Hg (mg.kg^{-1})	Cd (mg.kg^{-1})	Pb (mg.kg^{-1})	Cu (mg.kg^{-1})	Zn (mg.kg^{-1})
Markušovce	Soil content	7.0314	1.5600	26.4000	29.5000	71.5000
	Plant content	0.0234	0.1513	0.1220	1.8062	7.1031
	TF	0.0033	0.0970	0.0046	0.0612	0.0993
Matejovce nad Hornádom I	Soil content	10.0279	1.6700	32.2000	45.5000	81.4000
	Plant content	0.0227	0.0475	0.0250	2.1750	9.3500
	TF	0.0022	0.0284	0.0007	0.0478	0.1148
Matejovce nad Hornádom II	Soil content	3.040904	4.7000	56.3000	35.2000	156.9000
	Plant content	0.022661	0.0700	1.1500	1.8500	7.1000
	TF	0.0074	0.0148	0.0204	0.0525	0.0452
Poráč I	Soil content	2.503253	1.93	56	19.6	143.9
	Plant content	0.004327	0.145	0.175	1.2	8.7
	TF	0.001728	0.075129	0.003125	0.061224	0.060458
Poráč II	Soil content	5.150774	1.66	34.8	21.8	215.1
	Plant content	0.014414	0.2475	0.3	1.6	15.7
	TF	0.002798	0.149096	0.008620	0.073394	0.072989
Poráč III	Soil content	5.255338	1.47	26.5	58.7	161.8
	Plant content	0.009898	0.0725	0.1	1,525	14.9
	TF	0.001883	0.049319	0.003773	0.025979	0.092088
	Average of TF	0.003213	0.068957	0.006869	0.053682	0.080805

Table 2 the content of heavy metalls in sheep`s samples (mg.kg^{-1} fresh mater).

Samples		Hg [mg. kg^{-1} f.m.]	Cd [mg. kg^{-1} f.m.]	Pb [mg. kg^{-1} f.m.]	Cu [mg. kg^{-1} f.m.]	Zn [mg. kg^{-1} f.m.]
Sheep from Porač I	Meet	0.004839	0.105479 > LV	<DL	1.423975	26.369917
	Liver	0.019860	0.067940	<DL	84.765406 > LV	23.379426
	Kidney	0.132768 > LV	0.242073	0.094930	3.987089	16.565407
Sheep from Porač II	Meet	0.006589	0.004751	0.142558 > LV	1.330545	16.346702
	Liver	0.019866	0.959438 > LV	0.143199	5.262592	18.078975
	Kidney	0.100277	0.225430	<DL	3.641565	49.854771
Sheep from Matejovce nad Hornádom	Meet	0.001637	0.151804 > LV	<DL	1.567014	21.252632
	Liver	0.013885	0.231668	0.553988 > LV	84.659548 > LV	32.534246
	Kidney	0.064443	0.826528	<DL	3.761445	23.855481
Sheep Porač	Cheese	0.001636	0.075922 > LV	0.142355	0.332162	22.349814
	Cheese	0.001358	0.062233	0.047872	0.239360	21.063717
	Cheese	0.002970	<DL	0.058800	0.543000	27.940000

*DL – Detection Limit

* LV – Relevant limit value of the Food Codex SR

Samples exceeded the limit value for mercury (Hg max. 0.1 mg.kg^{-1}) were observed in the internal organs only in the case of kidney sheep from Porac I, by 1.3-fold. This corresponds well with the findings of **Kačmar et al**. (**1992**) and **Sharif et al.** (**2005**) who also recorded the highest accumulation of mercury in the kidney and the liver, and lower in meat. Their results indicate that long-term ingestion of feed contaminated with mercury leads to increased accumulation of mercury in the kidneys and liver.

Continued cadmium limits (Cd max 0,05 mg.kg^{-1}) were exceeded in the case of meat samples from Poráč I and Matejovce nad Hornádom, by 2.1-fold and 3-fold, respectively. In one sample of sheep cheese from Poráč III cadmium content exceeded the limit value for milk products (Cd max. 0.06 mg.kg^{-1}) by 1.26 times. Similar results were also recorded by **Anastasio et al. (2006)**. Lead transgress the limit value for meat (Pb max. 0.1 mg.kg^{-1}) in a sample of Poráč II, by 1.4 -fold. Also exceeded the limit value for internal organs (Pb max. 0.5 mg.kg^{-1}) in the liver of sheep from Matejovce nad Hornádom. Copper exceeded the limit value for internal organs (Cu max. 80 mg.kg^{-1}) in liver samples of sheep from Poráč I and Matejovce nad Hornádom over 1.5 times. The relationship between pasture contamination by heavy metals and their content in the organs of sheep have been also confirmed (**Smith et al., 2009**; **Akoto et al., 2014).**

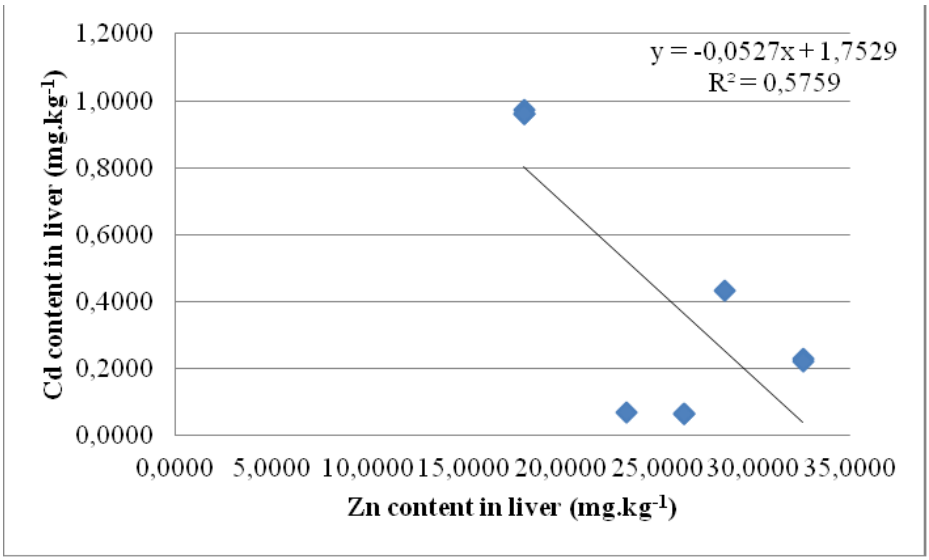

Figure 1 Comparison of Zn – Cd content
Confirmed the moderate correlation between total content of Zn in the liver of sheep and a reduction of total Cd. When will accumulate less Cd in liver of sheep concentration of Zn increases.

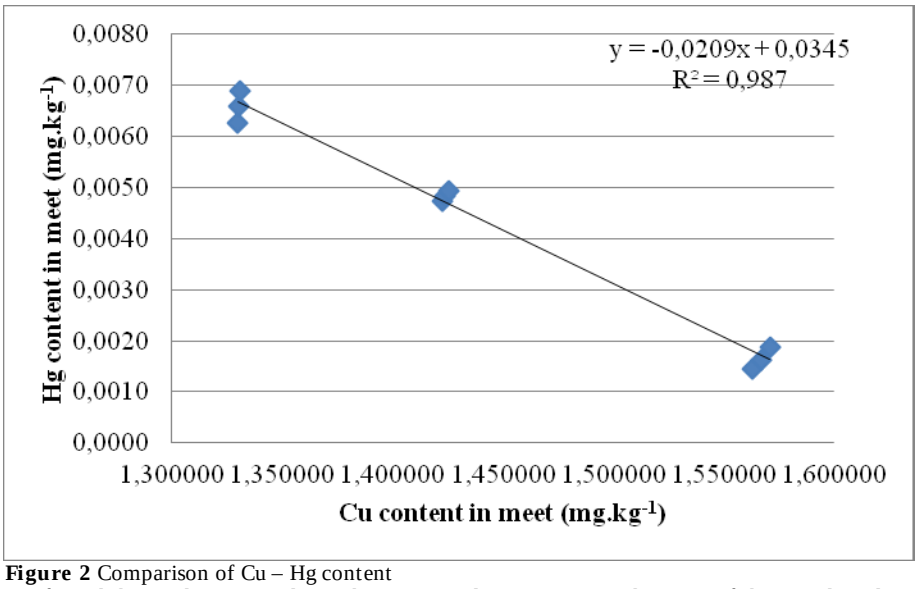

Figure 2 Comparison of Cu – Hg content
Confirmed the moderate correlation between total Cu content in the meet of sheep and total Hg concentration. When concentration of Cu in sheep meet will increase, the accumulation of Hg decreases.

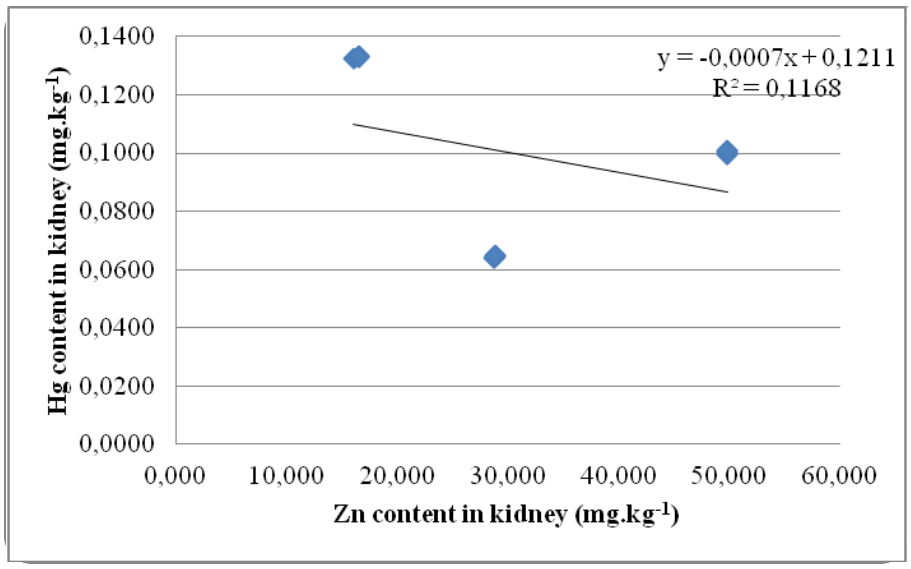

Figure 3 Comparison of Zn – Hg content
The suspected antagonism of Zn to Hg was not confirmed, so the increase in Zn content in the kidney of sheep was accompanied by higher Hg concentrations in the samples. Hg toxicity is manifested by displacement of elemental Zn from tissues.

CONCLUSION

Soil as a basic matrix of the local food chain, in addition to geochemical weathering of parent rock, is heavily burdened by air polluted by heavy metals from industrial production. For highly contaminated soil undergoing heavy metals in plants, as illustrated by the high levels of TF in order Zn> Cd> Cu> Pb> Hg. Food chains in Rudňany area contaminated with heavy metals, as evidenced by the their excessive concentrations in meat, internal organs and animal products. In the samples was recorded most frequently exceeding the limit value for cadmium 3 times. Also the highest exceedance of the limit value was observed in the case of cadmium in sample of meat from Matejovce ad Hornádom. Chronic toxicity of heavy metals may therefore translate to human health, therefore we do not recommend increased consumption of internal organs or meat produced in this area. In view of the toxicity of mercury, cadmium, lead by particular groups of people at risk, such as young children and pregnant women, their consumption should be excluded, respectively limited.

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