VETERINARSKI ARHIV 72 (5), 259-267, 2002

# Concentration of some heavy metals in cattle reared in the vicinity of a metallurgic industry

### Beáta Koréneková\*, Magdaléna Skalická, and Pavel Naď

Research Institute of Veterinary Medicine, University of Veterinary Medicine, Košice, Slovak Republic

### KORÉNEKOVÁ, B., M. SKALICKÁ, P. NAĎ: Concentration of some heavy metals in cattle reared in the vicinity of a metallurgic industry. Vet. arhiv 72, 259-267, 2002.

ABSTRACT

The occurrence of heavy metals was determined in the biological material of cattle slaughtered on agricultural farms in the fallout region of a metallurgical plant. In 1998, tissues and organs (n=42) from 21 cattle (muscle, liver) were analysed for the presence of Cd, Pb, Ni, Zn, Cu and Fe on an atomic absorption spectrophotometer (Unicam Solar 939, UK). The highest mean levels of heavy metals were recorded in the liver Pb 1.072; Cd 0.456; Zn 79.946; Cu 84.091; Fe 146.822; Ni 0.231 mg/kg, respectively. The highest mean levels in the muscle were Pb 0.671; Cd 0.126; Zn 81.180; Cu 6.312; Fe 51.800; Ni 0.350 mg/kg, respectively. From the results obtained concerning heavy metals in the area of observation, we can conclude that lead and cadmium are of particular ecological importance. We consider it necessary to implement ecological measures in the area of observation with respect to human consumption of beef.

Key words: heavy metals, cattle, environmental pollution

ISSN 0372-5480 Printed in Croatia

<sup>\*</sup> Contact address:

B. Koréneková, DVM., PhD. Research Institute of Veterinary Medicine, University of Veterinary Medicine, Komenského 73, 041 81, Košice, Slovak Republic, Phone: +421 55 63 318 52; Fax: +421 55 63 318 53; E-mail: korenekova@vuvm.sk

### Introduction

Metallurgical plants are involved in the general pollution of the environment by heavy metals. The largest steel producer (3,343,900 ton/ year) in the Slovak Republic is located in the surrounding area of Košice. Principal production programmes are steel plate products and other metal plates (IMRIŠ and KLENOVČANOVÁ, 1998). The farm animals (sheep and cattle) reared freely on pasture are the indicators of environmental pollution (GALLO et al., 1996). By respiration of polluted air (TATARUCH, 1995) and intake of contaminated feed (HRONEC, 1996), heavy metal bioaccumulates increasingly in organs and tissues of animals (TAHVONEN, 1996). Toxicity depends on animal species, and dose and length of their action upon the organism (MLYNARČÍKOVÁ et al., 1994). A higher occurrence of reproductive tract disorders (55.67%) is found in farms exposed to a metallurgical plant (MARAČEK et al., 1998) and are connected with functions of other organs, particularly liver (KOTTFEROVÁ, 1996).

The aim of the present study was to observe transfer of heavy metals into tissues and organs of cattle reared and kept in the area exposed to a metallurgical plant.

### Materials and methods

*Operational conditions.* In 1998, 42 samples (muscle, liver) of 21 cattle were taken from the vicinity of metallurgical plant (ESIW-East Slovakia Iron Works), and limited in order to detect the content of heavy metal. Cows with a mean age of 3 to 5 years came from Haniska, Cestice, Perín farms polluted by East Slovakia Iron Works (ESIW). Haniska farm lies 2 km northeast, Cestice 5.5 km southwest, and Perín 6 km south, of ESIW. The prevailing wind direction in that region is southwest. The samples of cattle tissue were immediately frozen and stored at -20 °C until analysed. Analysis consisted of digestion (5 ml HNO<sub>3</sub> and 1 ml HCl per 1g of sample) in a microwave oven (MILESTONE) and determination of heavy metal by the method of KOCOUREK (1992). Analysing reference materials (MBH ANAL Ltd., England) tested the reproducibility of the method. Samples were analysed for the presence of Cd, Pb, Ni, Cu, Zn and Fe using an atomic absorption spectrophotometer (AAS), UNICAM SOLAR 939,

U.K., with a graphite furnace with background correction. The flame condition and graphite furnace were optimised for maximum absorbency and linear response while aspirating known standards. The standards were prepared from the individual 1000 mg/kg standard (Merck, Germany); 100 ml of five combined standards were prepared in 0.1 N HNO<sub>3</sub>. The lamp current used was 75%. The signal type was transient for Cd, Pb, Ni, and continuous for Cu, Fe, and Zn. Measurement time was 3s. The recovery methods were 96-98% and reproducibility was better than 1.0%. All metal concentrations are expressed on a wet mass basis.

*Statistical analysis.* The statistical evaluation of the results has been done using the Microsoft Excel 7.0 program. Data are presented as mean, median, maximum and standard deviation (s.d.).

### Results

Muscle and liver samples of 21 cattle from an area polluted by a metallurgical plant were analysed for the presence of Cd, Pb, Ni, Zn, Cu and Fe (Table 1). The results obtained were compared with the maximum permissible hygiene limits according to the Codex Alimentorum, Slovak Republic No. 981/1996 for Cd, Pb, Ni, Cu, Zn in muscle (0.1; 0.4; 0.5; 5.0; 60 mg/kg) and liver (0.5; 1.0; 2.0; 80.0; 80.0 mg/kg) of cattle. Since maximum permissible hygiene limits for the Fe levels in cow muscles and liver has still not been approved in the Slovak Republic, the results of the analyses in the individual localities were compared with one another.

*Cadmium.* The limit values for muscle (0.1 mg/kg) were exceeded only in 1 sample from Perín. In this farm, the highest mean concentration of Cd (0.331 mg/kg) was observed in muscle samples. It is interesting to note very similar mean levels in muscle tissues in Haniska (0.024 mg/kg) and Cestice (0.023 mg/kg) farms. However, the situation was less favourable in the area of Cestice in assessing Cd concentration in cattle liver. This was evident from mean results (0,456 mg/kg) in this locality.

*Lead.* The values exceeding limit Pb in muscle were recorded in Cestice (0.416 mg/kg) and Haniska (0.671 mg/kg). Maximum Pb values were recorded in the sample of liver in the farm at Haniska (2.324 mg/kg). The

maximum values were exceeded in 13 samples of muscle and 4 samples of liver.

Element		Haniska		Cestice		Perín	
		Muscle	Liver	Muscle	Liver	Muscle	Liver
Cd	Max	0.06	0.161	0.037	0.184	0.300	0.491
	Median	0.021	0.070	0.023	0.387	0.086	0.306
	Mean	0.024	0.084	0.023	0.456	0.126	0.331
	s.d.	0.019	0.042	0.009	0.325	0.107	0.105
	n	7	7	6	6	8	8
Pb	Max	0.854	2.324	0.700	0.824	0.691	1.140
	Median	0.691	0.830	0.387	0.707	0.342	0.458
	Mean	0.671	1.072	0.416	0.729	0.386	0.544
	s.d.	0.146	0.636	0.171	0.057	0.237	0.261
	n	7	7	6	6	8	8
Ni	Max	0.210	0.244	0.899	0.394	0.527	0.605
	Median	0.155	0.200	0.196	0.213	0.102	0.112
	Mean	0.156	0.176	0.350	0.231	0.146	0.182
	s.d.	0.047	0.055	0.336	0.111	0.158	0.187
	n	7	7	6	6	8	8
Cu	Max	6.740	74.950	6.330	176.300	9.959	70.370
	Median	4.290	27.780	4.613	94.000	6.214	49.775
	Mean	4.572	31.067	4.433	84.098	6.312	50.848
	s.d.	1.506	26.079	1.700	60.615	2.003	17.061
	n	7	7	6	6	8	8
Zn	Max	39.300	135.500	110.400	189.500	124.100	108.200
	Median	21.755	73.080	75.300	124.730	84.805	61.415
	Mean	23.712	79.946	23.863	36.992	81.180	66.544
	s.d.	9.572	37.880	4.775	3.342	34.759	33.273
	n	7	7	6	6	8	8
Fe	Max	93.600	269.000	85.490	229.100	64.520	178.900
	Median	36.850	103.800	45.985	99.605	52.320	141.300
	Mean	51.290	125.226	49.133	125.735	51.800	146.825
	s.d.	27.495	68.947	23.862	55.362	9.032	15.648
	n	7	7	6	6	8	8

Table 1. Concentrations of Cd, Pb, Ni, Cu, Zn and Fe in biological samples of cattle from three regions (Haniska, Cestice, Perín) in Slovakia (mg/kg origin matter)

Table 1. Specification of myomorphus mammals examined by renoculture and microscopic agglutination acording to the trapping area with corresponding results

# B. Koréneková et al.: Concentration of some heavy metals in cattle reared in the vicinity of a metallurgic industry

*Copper*. Excess of copper limit values for muscle and liver was observed in samples of muscle (Perín 5; Cestice 3; Haniska 2) and liver (Cestice 4) of cattle. The highest Cu concentration was observed in liver (176.3 mg/ kg) in the farm at Cestice.

*Zinc.* During analyses, 14 above-limit samples of zinc in muscle were recorded altogether in the observed localities (Cestice 5; Perín 6; Haniska 3). The highest mean values were recorded in liver (79.946 mg/kg) and muscle (81.180 mg/kg) from the Haniska and Perin farms.

*Nickel*. Monitoring of the observed regions revealed 3 above-limit samples of Ni (Cestice 2; Perín 1). Highest mean Ni values were observed in liver (0.231; 0.176 mg/kg, respectively) at the Cestice and Haniska farms.

*Iron*. The highest mean Fe levels of liver in exposed herds were recorded in the locality of Cestice (125.735 mg/kg) and Haniska (125.226 mg/kg).

### Discussion

Evaluation of heavy metals levels in livestock is important for assessing the potential effects of pollutants on grazing cattle, and for quantifying contaminant intakes by humans. Essential elements, such as copper and zinc, are toxic when ingested in excess.

*Cadmium*. The results of our study are higher than mean Cd values in liver (0.112 mg/kg) observed in monitoring of the Slovak Republic by SOKOL et al. (1998). A monitoring program has been carried out with the purpose of avoiding the distribution of foodstuffs that could pose a risk to human health if consumed. It appears that intake of Cd by the observed cattle was elevated due to pollution from a metallurgical plant. Cadmium predominantly accumulates in the kidneys and the liver because its rate of elimination from these organs is relatively low. This is partly due to the binding of Cd to metallothionein in these tissues (GARCÍA - FERNANDEZ et al., 1996). In cattle from the polluted area, cadmium content of the liver and muscle was higher (mainly in the farms at Cestice and Perin) than those measured in other countries. Residue levels in the liver (0.097 mg/kg) and muscle (0.001 mg/kg) of cattle from Galicia (Spain) were low in comparison to our results (LOPEZ-ALONSO et al., 2000a).

*Lead.* The lead concentrations in muscle of cattle found in our study were greater than the values recorded by DOGANOC (1996), FALANDYSZ (1993), TAHVONEN and KUMPULAINEN (1995), who found the mean values in ruminant muscle of Pb (0.05; 0.04; 0.01 mg/kg, respectively) in Slovenia, Poland and Finland. Our values of Pb in liver are higher than data (0.239; 0.10 mg/kg, respectively) reported by JARC (1990) in Austria and DOGANOC (1996) in Slovenia. The results point to the fact that in the observed region of a metallurgical plant, lead acts as an important environmental contaminant.

*Copper.* It has been shown that levels of copper in liver were significantly higher than in muscle, mainly in the farms at Cestice and Perin. In the present study, higher values of copper were found in the liver and in the muscle than in other countries, e.g. Sweden - 39, 0.87 mg/kg (JOHREM et al., 1989) and Poland - 29, 1.2 mg/kg (FALANDYSZ, 1993). Higher mean Cu levels in liver can be caused by contamination of pasture and by industrial emissions. While swine are tolerant to an excess of Cu in their diet, sheep are extremely sensitive, and cattle to an intermediate level (TOKARNIA et al., 2000).

*Zinc.* The results of the present study indicate that values of muscle zinc in cattle were relatively high compared with those in the liver. Moreover, in the farm at Perin, these values were higher than in liver. According to LOPEZ-ALONSO et al. (2000b) muscle is one of the most important tissues for Zn accumulation, and possessed Zn concentrations that were similar those in the liver. Our study demonstrates that zinc concentrations in liver and muscle were higher than those reported for cattle in Sweden (40; 49 mg/kg) and Poland (42; 34 mg/kg) by JOHREM et al. (1989), and FALANDYSZ (1993). Both elements, Cu and Zn, accumulate in liver (BENEMARIYA et al., 1993) which was confirmed in the observed farms.

*Nickel.* Although Ni is considered an essential element, deficiency in animals is not anticipated since Ni intake generally exceeds its requirement. Daily intake of Ni in fodder supports this part of the organism, where there is storage (SUNDERMAN and OSKARSSON, 1991). Our results, obtained in the polluted area of the metallurgical plant, were higher and did not correspond with those obtained by ELLEN et al. (1989), who found the mean values in ruminant kidneys of 0.022 mg/kg and average content for liver in the other

tissues below 0.01 mg/kg fresh matter. On the other hand, the results of the present study are lower than results obtained by ANKE (1988) who reported 0.6 for liver.

*Iron*. The enhanced absorption of Cd and Zn in cattle in a contaminated area has an adverse effect on iron absorption (WENTINK et al., 1992). This testifies to a considerable accumulation of Fe in internal organs. It is of interest that relatively well-balanced Fe levels were recorded in all three observed localities in muscles of cattle.

The results obtained show that the contents of heavy metals in the vicinity of the metallurgical plant are ecologically important, mainly of Cd, Pb. The hygienic control of beef from the polluted area should be intensified with regard to human consumption.

With regard to the fact that in some samples maximum allowable limits for food were exceeded, effective ecological measures should be taken that would have a beneficial effect on the landscape and environment in the vicinity of metallurgical plant.

### References

- ANKE, M. (1988): Diagnosemöglichkeiten des Zink-, Mangan-, Jod-, Selen-, Molybden-Kadmium-, Nickel-, Lithium-, and Arsenstatus. Mengen und Spurenelemente 12, 364-368.
- BENEMARIYA, H., H. ROBBERECHT, H. DEELSTRA (1993): Zinc, copper and selenium in milk and organs of cow and goat from Burundi, Africa. Sci. Tot. Environ.128, 83-98.
- DOGANOC, D. Z. (1996): Lead and cadmium concentration in meat, liver and kidney of Slovenia cattle and pigs from 1989 to 1993. Food Add. Contam. 13, 237-241.
- ELLEN, G., J. W. VAN LOON, K. TOLSMA (1989): Copper, chromium, manganese, nickel and zinc in kidneys of cattle, pigs and sheep and in chicken livers in the Netherlands. Z. Lebensm. Unters. Forsch. 189, 534-537.
- FALANDYSZ, J. (1993): Some toxic and essential trace metals in cattle from the northern part of Poland. Sci. Tot. Environ. 136, 177-191.
- GALLO, M., R. MLYNÁR, L. RAJČÁKOVÁ (1996): Porovnanie obsahu ťažkých kovov v tkanivách dojníc zo Spišských Vlách a Ľubeníka. Sympozium o ekológii vo vybraných aglomeraciách Jelšavy a Ľubeníka a Stredného Spiša, Hrádok, pp. 29-31.
- GARCIA-FERNANDEZ, A. J., J. A. SÁNCHEZ-GARCIA, M. GÓMEZ-ZAPATA, A. LUNA (1996): Distribution of cadmium in blood and tissues of wild birds. Arch. Environ. Contam. Toxicol. 30, 252-258.

- HRONEC, O. (1996): Exhaláty priemyslu a ich ekonomické dôsledky na rastlinnú výrobu, Sympózium o ekológii vo vybraných aglomeraciách Jelšavy a Ľubeníka a Stredného Spiša, Hrádok, pp. 74-77.
- IMRIŠ, I., A. KLENOVČANOVÁ (1998): Vplyv hutníctva na Slovensku na životné prostredie, 98, Zborník, 18. Konferencia, Hutnícka analytika, Nízke Tatry, pp. 149-165.
- JARC, H. (1990): Rückstaduntersuchungen in Österreich, 3. Mitt.: Untersuchungen über Schwermetall, Pestizid- und Antibiotikrückstände in Schlachttieren aus Niederösterreich. Wien. Tierärztl. Mschr 67, 133-138.
- JOHREM, L., B. SUNDSTROM, C. ASTRAND, G. HAEGGLUND (1989): The levels of zinc, copper, manganese, selenium, chromium, nickel, cobalt and aluminium in the meat, liver and kidney of Swedisch pigs and cattle. Z. Lebensm. Unters. Forsch. 188, 39-44.
- KOCOUREK, V. (1992): Metódy stanovení cudzorodých látek v potravinách, Středisko potravinových informácií, Praha.
- KOTTFEROVÁ, J. (1996): Residual contaminants of cadmium in relation to environmental protection, health and quality of food products. Dissertation, Košice, pp. 130.
- LÓPEZ-ALONSO, M., J. L. BENEDITO, M. MIRANDA, C. CASTILLO, J. HERNANDEZ, R. F. SHORE (2000a): Toxic and trace elements in liver, kidney and meat from cattle slaughtered in Galicia (NW Spain). Food Add. Contam. 17, 447-457.
- LÓPEZ-ALONSO, M., J. L. BENEDITO, M. MIRANDA, C. CASTILLO, J. HERNANDEZ, R. F. SHORE (2000b): Arsenic, cadmium, lead, copper and zinc in cattle from Galicia (NW Spain). Sci. Tot. Environ. 246, 237-248.
- MARAČEK, I., L. LAZÁR, B. KORÉNEKOVÁ, J. CHOMA, V. DÁVID (1998): Rezíduá t'ažkých kovov a výskyt chorobnosti reprodukčných orgánov kráv v spádovej oblasti hutníckeho kombinátu. Slovak Vet. J. 23, 159-163.
- MLYNARČÍKOVÁ, H., J. LEGÁTH, N. PIJAKOVÁ (1994): Hodnotenie expozície vo vzťahu k hodnoteniu miery rizika chemických látok. Slovak Vet. J. 19, 291-293,
- SOKOL, J., J. KUBINEC, I. BREYL, J. KOŠUTZKÝ (1998): Koncentrácia kadmia v surovinách živočíšneho pôvodu, vybraných potranách a v krmivách v Slovenskej Republike v rokoch 1990 - 1996. Slovak Vet. J. 23, 142-146.
- SUNDERMAN, F., W. A. OSKARSSON (1991): Metals and their compounds in the environment. VCH Verlagsgesellschaft mbH, Weinheim 25, 1101-1126.
- TAHVONEN, R. (1996): Contents of lead and cadmium in foods and diets. Food Rev. Intern. 1, 1-70.
- TAHVONEN, R., J. T. KUMPULAINEN (1995): Contents of lead and cadmium in foods in Finland. Proceedings of Trace Elements Natural Antioxidant and Contaminants, Helsinky, pp. 85-96.

- TATARUCH, F. (1995): Red deer antlers as biomonitors for lead contamination. Bull. Environ. Contam. Toxicol. 55, 332-437.
- TOKARNIA, C. H., J. DOBEREINER, P. V. PEIXOTO (2000): Outbreak of copper poisoning in cattle fed poultry litter. Vet. Human Toxicol. 42, 92-95.

WENTINK, G. H., Th. WENSING, B. G. F. KESSELS (1992): Toxiciteit van cadmium voor rundvee. Tijdsch. Diergeneeskd. 17, 548-550.

Received: 17 February 2000 Accepted: 30 October 2002

#### KORÉNEKOVÁ, B., M. SKALICKÁ, P. NAĎ: Koncentracija nekih teških metala u goveda uzgajanih u blizini metalurških središta. Vet. arhiv 72, 259-267, 2002. SAŽETAK

Nalaz teških metala istra•en je u tkivu zaklanih goveda prethodno uzgajanih u blizini metalurških središta. Koncentracije Cd, Pb, Ni, Zn, Cu i Fe bile su određene metodom atomske apsorpcije (Unicam Solar, 939) u mišićnom i jetrenom tkivu 21 goveda. Najveće srednje vrijednosti utvrđene su u jetri i to za Pb 1,072 mg/kg, Cd 0,456 mg/kg, Zn 79,946 mg/kg, Cu 84,091 mg/kg, Fe 146,822 mg/kg i Ni 0,231 mg/kg. Utvrđene su i najveće prosječne vrijednosti u mišićnom tkivu koje su za Pb iznosile 0,671 mg/kg, Cd 0,126 mg/kg, Zn 81,180 mg/kg, Cu 6,312 mg/kg, Fe 51,800 mg/kg i Ni 0,350 mg/kg. Zaključeno je da Cd i Pb imaju najveće značenje te da se mora uspostaviti trajni nadzor kojim bi se odredio rizik za potrošače.

Ključne riječi: teški metali, govedo, zagađenje okoliša