Bull. Environ. Contam. Toxicol. (2005) 74:740–744

DOI: 10.1007/s00128-005-0644-9

Bulletin of Environmental Contamination and Toxicology

Copper in Livestock from Polluted Area

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Received: 20 October 2004/Accepted: 12 January 2005

Heavy metals together with pesticides from emissions are dominant compounds of the chemical load on the environment of man and animals (Kottferová 1996; Pistl *et al.* 2003). Copper is an essential but potentially toxic element. Deficient intake results in impairment of various biological functions but the metal is toxic when ingested in excess (Underwood 1999). Copper is involved in carbohydrate and lipid metabolism and in immune function (Bíreš *et al.* 1997; Solyak *et al.* 2001a,b). Copper has a multiple function, as iron absorption, haemopoesis, various enzyme activities and in the oxidation-reduction process (Rous and Jelinek 2000). Trace element metabolism is itself affected by toxic metals. Disturbances in the homeostasis of essential elements may, in fact, be one mechanism of toxicity (Liu *et al.* 1992). Knowledge of the levels of Cu in livestock is important for assessing the potential effect of pollutants on domestic animals themselves and in quantifying contaminant intake in humans (Gallo *et al.* 1996; Massanyi *et al.* 2000). The objective of this study was to determined the copper contents in livestock from a polluted area of metallurgical plant from Eastern Slovakia (Slovak Republic).

MATERIALS AND METHODS

In 1995-1999, 124 samples (muscle, heart, liver and kidney) of cattle (cows) were taken from area (Figure 1) located in 5.5 km of metallurgical plant in Eastern Slovakia (Slovak Republic). The prevailing wind direction in that region is south-west. This was done to ensure that the sample collected was representative of the polluted region. Cattle were the predominant type of livestock in this area. Cows were between 3 and 5 years old. All were healthy at the time of slaughter. The samples were collected at time of slaughter and immediately transported to the laboratory where they were frozen and stored at -20° C until analysed. The analysis consisted of digestion (5 ml HNO_3 and 1 ml HCl per 1g of sample) in the microwave oven Milestone and determination of Cu 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 Cu using an atomic absorption spectrophotometer, (Unicam Solar 939) at wavelength 324.8 nm. The flame conditions were optimised for maximum absorbance 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_3. The signal type was continuous for Cu. Measurement time was 3s. The recovery methods were 96-98% and reproducibility

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was better than 1.0%. Quantification limit was 0.096 $mg.l^{-1}$ and detection limit was 0.29 $mg.l^{-1}$. Copper concentrations were expressed on a wet weight (w.wt.).

The statistical evaluation of the results was done with Microsoft Excel 7.0. Data were presented as mean, maximum, and standard deviation. Non detectable residues were not included.

RESULTS AND DISCUSSION

The variation in the copper content in tissues of cattle from polluted area in 1995-1999 is shown in Table 1.
In 1995, the lowest mean Cu level (0.482 mg/kg w.wt.) were observed in muscle. Similar low mean levels were also recorded for Cu in 1996 and 1997 (0.793; 0.509 mg/kg w.wt.), respectively. On the other hand, in 1998 higher mean levels of Cu was found (6.312 mg/kg) when compared with previous years. This mean value exceeded permitted limits for copper in muscle tissue (5.0 mg/kg).

Relatively low mean Cu levels were determined in heart in years 1995-1999. However, in years 1998 and 1999 were recorded slightly increased concentrations of Cu levels.
The consistently higher Cu levels were detected in liver during years 1995-1999. The values reported in this paper in year 1999 are higher than highest permissible hygienic limit the (Codex Alimentorum of the Slovak Republic No. 98/1996) for copper in inner organs (60.0 mg/kg). In this year was recorded the maximum value of Cu 160.30 mg/kg w.wt. in polluted area.

The mean value of Cu in kidney were ranged from 2.757 mg/kg w.wt. to 8.350 mg/kg w.wt. in years 1995 and 1998. The data show that Cu accumulated mainly in the liver of cows, from observed polluted area. It has been also shown that levels of copper in liver were higher in Slovakia than in the other countries. The mean values of copper were found e.g. in Sweden - 39 mg/kg (Johrem *et al.*1996), in Poland - 29 mg/kg (Falandysz 1993), in Spain - 60.3 mg/kg (López Alonso *et al* . 2000).

According to Benemariya *et al.* (1993) copper accumulate mainly in the liver. Ruminants have a superior capacity to bind copper in the liver and have relatively poor copper excretion. The characteristic of high copper storage capacity in ruminants means that they are likely to be good biomonitors of environmental copper levels and can be used to identify areas of copper contamination. This was demonstrated by a study of López Alonso *et al.* (2002).

Cattle from the industrialised area of metallurgical plant showed higher hepatic copper concentrations in years 1997 - 1999 than years 1995 and 1996. The obtained mean levels in years 1997 - 1999 were highest than permissible hygienic limit for liver in the Slovak Republic (60.0 mg/kg).

When copper concentrations for cattle from different countries were compared, it was apparent that muscle copper levels in East Slovakia animals were approximately

Table 1. Concentration of copper in the muscle, liver, heart and kidney (mg/kg w wt.) in Slovak cattle from polluted area

Years		Muscle	Liver	Heart	Kidney
	n	6	6	6	6
1995	x	0.482	10.975	2.255	2.757
	x max	0.711	37.750	2.853	3.619
	Sd	0.21	14.167	0.789	1.222
	limit	0	0	0	0
	n	7	7	7	7
1996	x	0.793	23.604	3.232	4.039
	x max	1.109	38.800	3.719	5.815
	Sd	0.174	10.205	0.268	0.909
	limit	0	0	0	0
	n	6	6	6	6
1997	x	0.509	41.143	2.946	4.084
	x max	1.135	74.860	3.455	5.100
	Sd	0.467	26.802	0.365	0.849
	limit	0	1	0	0
	n	6	6	6	6
1998	x	6.312	50.484	8.116	8.350
	x max	9.959	70.370	14.250	13.230
	Sd	2.003	17.061	3.206	2.831
	limit	5	2	0	0
	n	6	6	6	6
1999	x	1.872	94.821	8.558	6.880
	x max	3.820	160.30	13.750	9.928
	Sd	1.109	74.685	3.103	3.265
	limit	0	5	3	0

n, number of samples analysed; *x*, arithmetic mean; *x max*, maximal values; *Sd,* standard deviation; *limit*, number of samples accessed permissible hygienic limit for copper

5 x in year 1998 than that in cattle elsewhere. It has been found that levels of copper in muscle were 1995,1996,1997,1999 similar than in the other countries. The mean values of copper were found e.g. in Sweden - 0.87 mg/kg (Johrem *et al.*1996), in Poland - 1.20 mg/kg (Falandysz 1993), in Spain - 1.26 mg/kg (López Alonso *et al.* 2000). According to Underwood (1999), levels of copper in most

Figure 1. Map of Slovak Republic

tissues, except muscle and endocrine organs, are directly affected by copper intake, tend to decline with age, and are quite species-dependent

In contrast to the muscle, copper concentrations in the kidney of cows from East Slovakia were higher, but were similar to those in animals from elsewhere in years 1995-1997. The mean values of copper were recorded e.g. in Sweden - 3.70 mg/kg (Johrem *et al.*1996), in Poland - 5.60 mg/kg (Falandysz 1993), in Spain - 3.60 (López Alonso *et al.* 2000). The similar results were observed also in the heart of cows.

Cadmium exposure has an adverse effect on hepatic and renal copper storage (Yang *et al.* 2000; Roesijadi 2000). According to Grosicky and Kowalski (2001) a copper fortified diet increased the absorption of cadmium from the gastrointestinal tract and the bodily and organ cadmium burden. On the other hand, an increase in body weight gain produced by the copper supplemental diet suggested that toxic action was limited.

The results of this study show that higher mean copper concentrations in cattle were influenced by contamination of pasture with industrial sources of pollution. The implementation of systematic biomonitoring programme to better evaluate the state and trends of metal contamination is necessary.

REFERENCES

Benemariya H, Robberecht H, Deelstra H (1993) Zinc, copper and selenium in milk and organs of goat from Burundi, Africa. Sci Total Environ 128: 83-98

Bíreš J, Bartko P, Huska M.(1997) Distribution of risk elements in the organism of sheep after industrial intoxication with zinc. Spectros Lett 30: 1236 – 1237

Codex alimentorum of the Slovak Republic No. 981/1996. Decree of the Ministry of Agriculture of Slovak Republic and Ministry of Health of the Slovak Republic

Falandysz J. (1993) Some toxic and essential trace metal in cattle from the northern part of Poland. Sci Total Environ 136: 177-179

Gallo M, Gallo J, Sommer A, Flak P (1996) Influence of emission fall-out movement of heavy metal in the cycle soil, plant, animal. Arch Tierz Dummerstorf 39:195-202

Grosicky A, Kowalski B (2001) Absorption and distribution of cadmium in rats fed a copper enriched diet, Bull Vet Inst Pulawy 45: 333-339

Jorhem L, Sundstrom B, Engman J, Astrand C and Olsson I. (1996) Levels of certain trace elements in beef and pork imported to Sweden. Food Addit Contam 13:737-745

Kocourek V (1992) Method's of analysis residues substance in food. Praha, Czech republic

Kottferová J (1996) Residual contaminants of cadmium in relation to environmental protection, health and quality of food products. Dissertation work, UVM Košice, Slovak Republic 130

Liu X, Nordberg GF, Jin T (1992) Increased urinary excretion of zinc and copper by mercury chloride injection in rats. Biometals 5: 17-22

López Alonso M, Beneditto JL, Miranda M, Castillo C, Hernández J, Shore RF (2000) Aresnic, cadmium, lead, copper and zinc in cattle from Galicia. NW Spain Sci Total Environ 246: 237-248

López Alonso M, Beneditto JL, Miranda M, Castillo C, Hernández J, Shore RF (2000) Toxic and trace elements in liver, kidney and meat from cattle slaughtered in Galicia. (NW Spain) Food Addit Contam 17: 447-457

López Alonso M, Benedito L, Miranda M, Castilo C, Hernandez J, Shore R.F (2002) Cattle as biomonitors of soil arsenic, copper, and zinc concentrations in Galicia (NW Spain), Arch. Environ. Contam Toxicol 43: 103-108

Massanyi P, Trandzik J, Lukac N, Strapak P, Kovacik J, Toman R. (2000) The contamination of bovine semen with cadmium, lead, copper and zinc and its relation to the quality of spermatozoa used for insemination. Folia Vet 44 :150-153.

Pistl J, Kovalkovičová N, Holovská V, Legath J, Mikula I (2003) Determination of the immunotoxic potential of pesticides on functional activity of sheep. Toxicology, 188: 73-81

Roesijadi G (2000) Metal transfer as a mechaism for metallothionein – mediated metal detoxification. Cellular Mol. Biol 46: 393-405

Rous P, Jelinek P (2000) The effect of increased soil contamination with heavy metals on their content in some rabitt tissues. Cz J Anim Sci 45: 319-324

Soylak M, Narin I, Elci L, Dogan M (2001a) Atomic absorption spectrometric determination of copper, cobalt, cadmium lead, nickel and chromium in table salt samples after preconcentration on activated carbon. Kuwait J Sci Eng 28:361-370

Soylak M, Elci L, Divrikli U, Saracoglu S (2001b) Monitoring trace metals levels in Kirsehir Turkey : serum copper and zinc levels of healthy subject. Fresenius Environ Bull 10: 329-330

Yang XF, Wang SY, Zhao RC, Ao SQ, Wang XR.(2000) Changes in tissue metals after cadmium intoxication and intervention with chlorpromazine in male rats. Biomed Environ Sci 13: 19-25

Underwood E J, Suttle A F. (1999) The mineral nutrition of livestock, 3rd Edition CABI Publishing, UK 586