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Essential Elements in Environmental Samples from Selected Regions in Slovakia

M. Ursínyová, V. Hladíková

Institute of Preventive and Clinical Medicine, Limbova 14, 833 01 Bratislava, Slovak Republic

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Zinc (Zn) and copper (Cu) belong to the essential elements ubiquitous in the environment at trace levels. Numerous sources of Zn and Cu occur (e.g., mining, smelting, electroplating, coal and oil combustion, waste incineration) and those anthropogenic activities can induce occupational risks and a redistribution of Zn and Cu among the different components of the environment. The judgement of consequences of Zn and Cu pollution is particularly difficult to make since Zn and Cu are essential trace elements (i.e., indisperable to life at low levels) and become toxic only at higher doses. Moreover, toxicological effects due to Zn and Cu are often difficult to differentiate from those due to accompanying impurities such as other trace elements (e.g., Cd and Pb) (Amiard and Amiard-Triquet 1993, US EPA 1987).

In our previous study we evaluated the contents of cadmium, lead and mercury in dustfall and soil, and their transport to vegetables and fruits. On the basis of the data from Food Basket we calculated the weekly intake of those toxic elements via vegetables and fruits, as well (Ursínyová et al. 1997).

The purpose of this work is to present the results of a study on the levels of Zn and Cu in soils and dustfall from selected regions of Slovakia affected by industrial and agricultural activities, and the absorption of the metals from soils to plants grown in the studied areas.

MATERIALS AND METHODS

The crops, the soil where they had been grown and dustfall were sampled from 28 main production areas in 5 localities during a period of 4 years.

Localities:
1. oil refinery and petrochemical complex (Slovnaft - Bratislava)
2. city in industrial region with 400 000 inhabitants (Bratislava)
3. town in agricultural region with 20 000 inhabitants (Dunajská Streda)
4. spa (Piešt'any)
5. mountain region with recreation facilities (Bezovec)

A total of 50 samples of each of the studied materials in each area were analyzed. Agricultural crops were selected according to their importance for consumption. In this way, a wide selection of crops such as leafy-, root-, bulb- and fruiting vegetables and fruits was obtained. The strategy of sampling and

Correspondence to: M. Ursínyová

preparing of materials for analyses was previously described (Ursínyová et al. 1997).

Zn and Cu were determined by atomic absorption spectrophotometry using Perkin-Elmer 5000 apparatus with air-acetylene flame. The measurements were carried out at the wavelengths of 213.9 nm for Zn and 324.7 nm for Cu. In the course the analytical work, at least one blank was run and analyzed for the corresponding elements together with each series of ten samples. The limits of detection (concentration corresponding to 3xSD of the blank) were for Zn 0.65 $mg.kg^{-1}$ in dustfall, 0.33 $mg.kg^{-1}$ in soil and crops; for Cu 2.05 $mg.kg^{-1}$ in dustfall, 1.03 $mg.kg^{-1}$ in soil and crops, respectively.

Standard reference materials (SRM) Tomato leaves 1573 from National Bureau of Standards (NBS), USA and Copper smelting plant flue dust (KHK), Lucerna P-Alfalfa, Wheat bread flour (p-WBF) and Rye bread flour (p-RBF) from the Institute of Radioecology and Applied Nuclear Techniques, Slovakia, were analyzed for the confirmation of the results. A summary of these control results is presented in Table 1.

Table 1. Results of measured concentrations of metals in SRM

Material	Element	Mean value ($\mu g.g^{-1}$)	Certified value ($\mu g.g^{-1}$)
Copper smelting plant flue dust	Zn	5.65 ± 0.15	5.67 - 5.86
	Cu	19.50 ± 0.35	19.2 - 19.7
Tomato leaves (NBS 1573)	Zn	60.5 ± 5.1	62 ± 6
	Cu	10.5 ± 1.0	11 ± 1
Lucerna P - alfalfa	Zn	31.0 ± 0.6	32.3 ± 34.2
	Cu	12.3 ± 0.4	10.9 ± 12.4
Wheat bread flour	Zn	17.5 ± 1.1	17.1 - 18.6
	Cu	2.75 ± 0.58	2.64 - 2.89
Rye bread flour	Zn	17.3 ± 0.6	15.5 - 16.6
	Cu	3.20 ± 0.11	2.28 - 2.59

RESULTS AND DISCUSSION

There are no administrative regulations concerning the content of metals in dustfall or the dust deposition of metals in Slovakia, nor were such regulations issued by WHO.

According to previously reported values (Luft und Gesundheit 1992) the average annual dust deposition of Zn in 27 different localities of Bavaria (FRG) varied between 30.2-185.0 $\mu g.m^{-2}.d^{-1}$ depending on the locality. The dust deposition of Cu reported in the same work ranged between 6.84 - 143.61 $\mu g.m^{-2}.d^{-1}$.

Our findings of minimum and maximum dust depositions of the Zn and Cu also varied in the different localities (Table 2) but the ranges of Zn values in all the localities studied were wider than those reported from Bavaria. In all the 5 localities, the maximum Zn values were considerably higher than those in Bavaria. The found elevated dust deposition of Zn in Slovakia in comparison to that in Germany was in a good agreement with the data of Zn deposition reported as the content of Zn in the moss species by Markert et al. (1996). Our findings of dust deposition of Cu were comparable to the Bavarian values. Median depositions of Zn and Cu are shown in Figure 1.

Table 2. Zn and Cu dust depositions (µg. m^{-2}. d^{-1})

Element	Locality									
	1		2		3		4		5	
	min	max	min	max	min	max	min	max	min	max
Zn	144	709.7	47.3	1307.3	83.3	1293	167	1171.7	92.3	1614.6
Cu	3.97	23.03	3	273.33	4.83	24.63	2.87	9.63	1.47	7.7

1 - Slovnaft, 2 - Bratislava, 3 - Dunajská Streda, 4 - Piešťany, 5 - Bezovec

The Maximum permissible concentrations of metals in agricultural soil in the Slovak Republic are 3000 mg.kg^{-1} and 500 mg.kg^{-1} for Zn and Cu, respectively. These limits are applicable for removal of elements from soil. The natural levels of metals in soil in geological conditions of Slovak territory are 140 mg.kg^{-1} and 36 mg.kg^{-1} for Zn and Cu, respectively (MP SR 1994).

The contents of the studied metals in air dried soil samples from the localities 1 - 5 are summarized in Table 3. Median contents of Zn and Cu in air dried soil in the localities under study are shown in Figure 2. The median values in these localities did not exceed the parameters given in the official material (MP SR 1994) as natural concentrations.

Table 3. Zn and Cu contents in air dried soil (mg.kg^{-1})

Element	Locality									
	1		2		3		4		5	
	min	max	min	max	min	max	min	max	min	max
Zn	25.4	119.5	28.8	171.1	23.7	136.5	43	120.5	28.7	119.7
Cu	11	34	14.5	40	13.6	44.6	18	45	17.4	43

1 - Slovnaft, 2 - Bratislava, 3 - Dunajská Streda, 4 - Piešťany, 5 - Bezovec

The edible crops were collected only from the localities 2, 3 and 4. The refinery and petrochemical complex in Slovnaft - Bratislava (locality 1) and mountain region Bezovec (locality 5) are the territories without agricultural activities. The contents of the metals in vegetables and fruits calculated on dry weight are summarized in Table 4. Median contents of Zn and Cu in vegetables and fruits are shown in Figure 3. The range (minimum - maximum) of the levels of essential metals in selected vegetables and fruits calculated on dry weight basis is presented in Table 5. Median contents of Zn and Cu in selected vegetables and fruits are shown in Figure 4. The zinc and copper levels in vegetables and

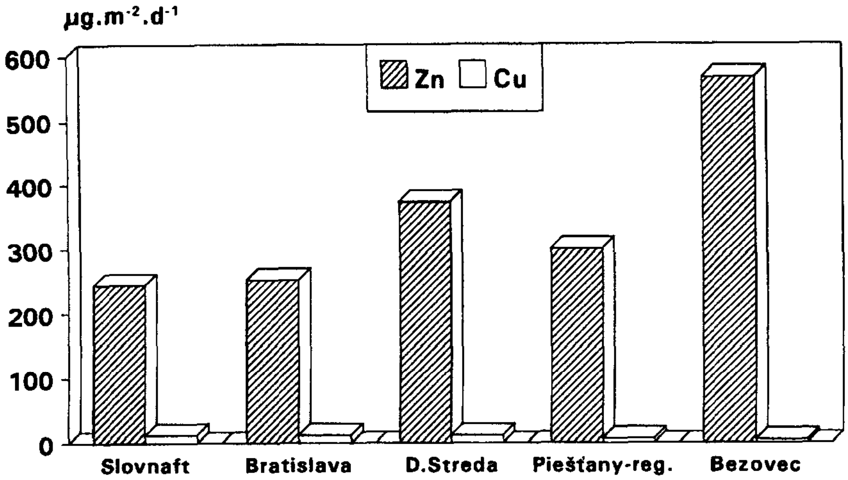

Figure 1. Median Zn and Cu dust depositions

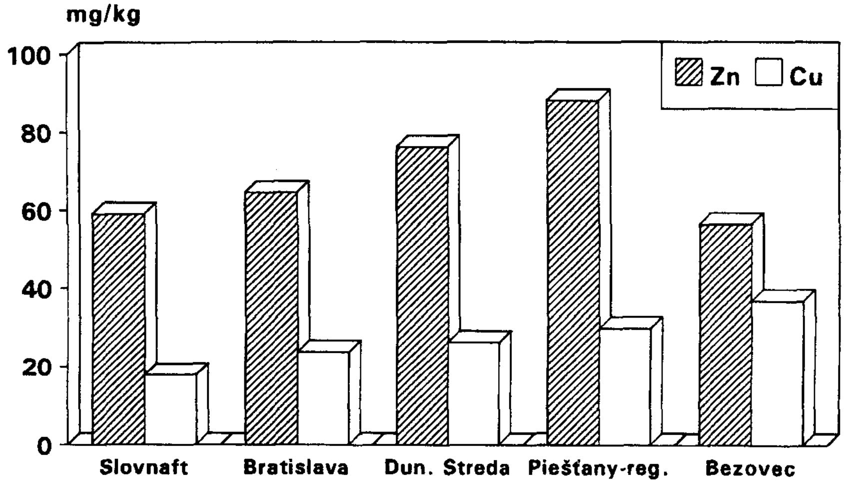

Figure 2. Median Zn and Cu concentrations in air dried soil

fruits in this study agree well with the reported values (Friberg et al. 1986). The levels of zinc and copper, and in vegetables and fruits calculated to fresh weight did not exceed the Maximum permissible levels given by Slovak regulations (Z.z. SR 1993). The correlations between the concentrations of Zn and Cu in vegetables and fruits and their concentrations in soil, resp. their dust deposition, were not found.

The median concentrations of Zn and Cu found in the crops were used to calculate their daily intakes from the vegetables and fruits, resp. On basis of the data from Food Basket of the Czech Republic (Ruprich et al. 1993) the daily consumption of vegetables and fruits per person was 209.529 g and 104.798 g, respectively, which corresponds to 11.0 % and 5.5 % of the total food consumed. It can be expected that the situation in Slovakia is quite similar.

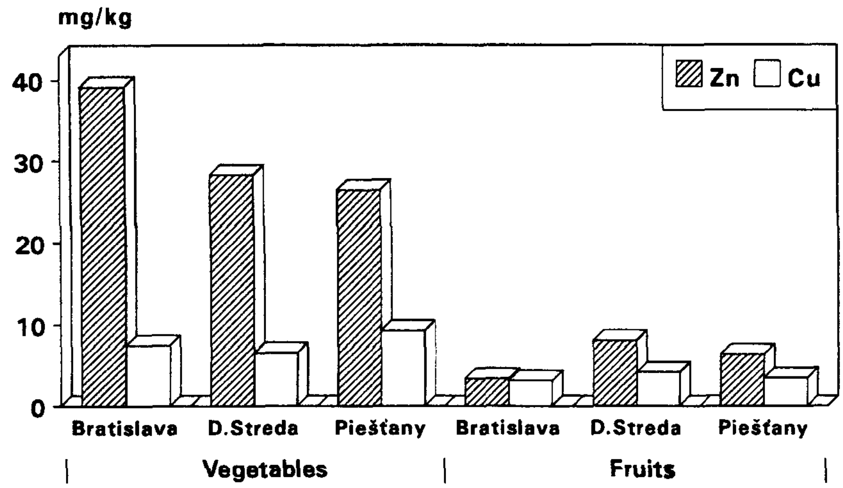

Figure 3. Median Zn and Cu concentrations in vegetables and fruits

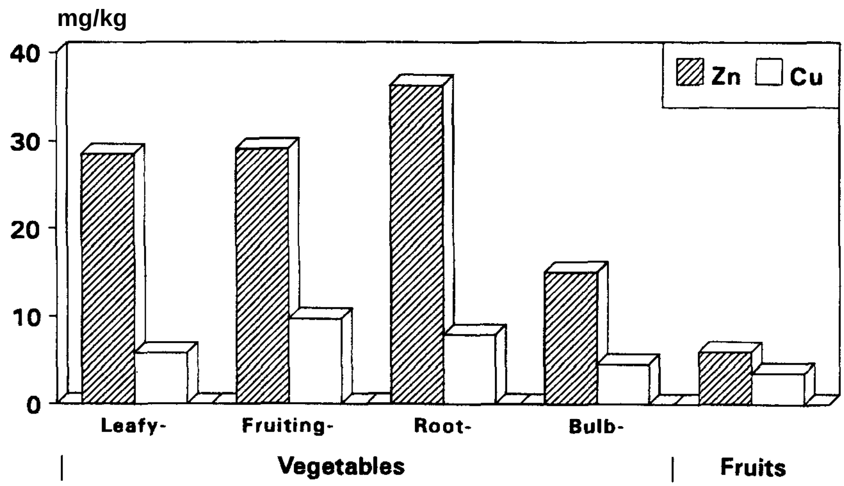

Figure 4. Median Zn and Cu concentrations in selected vegetables and fruits

Table 4. Zn and Cu contents in vegetables (mg.kg^{-1} d.wt.)

Crops	Element	Locality					
		2		3		4	
		min	max	min	max	min	max
Vegetables	Zn	13.2	63	15.9	45.5	8.1	96
	Cu	1.1	16	1.4	15.9	1.1	15.4
Fruits	Zn	1.2	13.5	2.4	18.5	2	18.4
	Cu	ND	15	2.8	11.2	1.5	13.5

2 - Bratislava, 3 - Dunajská Streda, 4 - Piešťany, *ND - Not detectable*

Table 5. Zn and Cu contents in vegetables and fruits ($mg.kg^{-1}$d.wt.)

Vegetables	Zn		Cu	
	min	max	min	max
Leafy-	13.2	63	1.1	14.6
Fruting-	13.7	61	3.1	16.6
Root-	14.9	96	3.1	15.4
Bulb-	8.1	34.4	3.2	9.3
Fuits	1.2	18.5	ND	15

ND - Not detectable

The calculated median daily intakes of essential elements from vegetables and fruits were as follows Zn - 1712 µg from vegetables and 189 µg from fruits; Cu - 440 µg from vegetables and 113 µg from fruits. The recommended intakes (Or-ten and Neuhaus 1984) are 15 000 µg Zn/day and 2 000 - 3 000 µg Cu/day. The contents of essential elements indicate that the daily intake of Zn was secured to 11.4 % from vegetables and to 1.3 % from fruits; Cu to 17.6 % from vegetables and to 4.5 % from fruits. Thus, the generally low consumption of vegetables and fruits in Slovak population also results in relatively low intakes of the essential elements.

However, it has to be kept in mind that all the above calculations are based on metal contents found in the crops grown in the localities under study. In reality, in the Slovak Republic, the values might be influenced by the consumption of imported crops where contents of the respective metals may be different.

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