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Toxic Elements in Environmental Samples from Selected Regions in Slovakia

M. Ursinyová, V. Hladiková, J. Uhnák J, Kovacicová

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

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The excessive content of toxic elements in the human environment is associated with the etiology of a number of diseases, especially with cardiovascular, kidney, nervous as well as bone diseases (Friberg et al. 1986). Cadmium (Cd), lead (Pb) and mercury (Hg) belong to those heavy metals posing the greatest hazard to human health. Therefore, monitoring of their levels in human environment is required (Corn 1993).

The purpose of this work is to present the results of a study on the levels of toxic metals 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. The findings of metals were compared with data by other authors and with the respective guidelines (Luft und Gesundheit 1992; Technical Report 1978, 1993; MP SR 1994).

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 (1988 - 1992).

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 (Pieštany)
5. mountain region with recreation facilities (Bezovec)

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 collected quantities were sufficient to provide a representative sample, i.e. 2 kg of plants and fruits per sample. The soil samples were taken from the upper 0 to 30 cm layer.A total of 50 samples of each of the studied materials in each area were analyzed. Thus, the total number of samples analyzed was 750.

Correspondence to: M. Ursínyová

Dustfall samples of 0.2 1 g and soil samples of 2 g were wet mineralized using the mixture of $HNO_3 HClO_4$ and H_2O_2 (Pal'ušová et al. 1991). The edible parts of the crops, as used for human consumption, were washed with bidistilled water, dried at 50°C, and homogenized. Wet digestion of 2 g homogenate was carried out in a closed digestion apparatus. After the digestion, solutions were made up to 50 mL with bidistilled water and stored in polyethylene bottles.

The Pb and Cd levels were determined by AAS method using Perkin-Elmer 5000 spectrophotometer with electrothermic atomizer HGA-500, autosampler AS 40 and printer PR-10. Pb and Cd were determined by flame technique with air-acetylene flame in soil and dustfall and by flameless atomization in vegetables and fruits. The measurements were carried out at the wavelength of 283.3 nm for Pb, 228.8 nm for Cd. Tables 1 and 2 show parameters of instrumental conditions at the determination of Pb and Cd in vegetables and fruits.

Hg levels in crops were analyzed directly without a wet procedure by the amalgamation technique using the TMA - 254 apparatus - Tesla Holešovice. Samples of dustfall and soil were mineralized by wet process and then Hg was determined by the amalgamation technique.

lo 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 3 x SD of the blank) were for Cd 0.0002 $mg.kg^{-1}$ in dustfall, 0.0004 $mg.kg^{-1}$ in soil and crops; for Pb 0.009 mg.kg -I in dustfall, 0.018 $mg.kg^{-1}$ in soil and crops; for Hg 0.0040 $mg.kg^{-1}$ in dustfall, 0.0083 $mg.kg^{-1}$ in soil and 0.0010 $mg.kg^{-1}$ in crops.

Standard reference materials (SRM) Tomato leaves 1573 from National Bureau of Standards (NBS), USA and Copper smelting plant flue dust (KHK) and Wheat bread flour (p-WBF) from 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 3.

RESULTS AND DISCUSSION

There are no administrative regulations concerning the content of metals in dustfall in Slovakia, nor were such regulations issued by WHO. The only available regulation is the technical directive for the prevention of air pollution in the FRG, TALuft (Luft und Gesundheit 1992). According to TALuft, Maximum permissible amounts of Cd and Pb in dustfall are 5 and 250 $\mu gm^{-2}.d^{-1}$, respectively. The content of Hg in dustfall are not limited by TALuft.

Our tidings of the Cd, Pb, and Hg levels in dustfall varied in the different localities (Table 4). The Cd and Pb levels found in dustfall showed that maximum Cd level in locality 1 was higher (6.13 $\mu g.m^{-2}.d^{-1}$) than the Maximum permissible amounts by TALuft and the maximum content of Pb in the same locality (1310 $\mu g.m^{-2}.d^{-1}$) exceeded 5 times the Maximum permissible amounts by TALuft.

Table 1. Instrumental conditions for determination of Cd

Element	Temperature program						
		Step 1	Step 2	Step 3	Step 4	Step 5	Step 6
Cd	Temp.(°C)	90	100	130	500	1300	2200
	Ramp (sec)	10	5	5	20	0	0
	Hold (sec)	15	5	10	15	3	3
	Ar flow (mL/min)	300	300	300	300	0 MP,RD	300 MP

MP: Temperature-Controlled Maximum Power Heating
RD: Read

Wavelength: 228.8 nm
Slit width: 0.7 nm
Lamp current: 7.2 mA
Background correction: on
Graphite tube: pyrolytically coated
Measurement: peak height
Injection volume: 20 µL of sample + 10 µL of modifier $NH_4H_2PO_4$
Standards: 2,4, 6 $\mu g.L^{-1}$ of Cd iu 2% V/V nitric acid

Table 2. Instrumental conditions for determination of Pb

Element	Temperature program						
		Step 1	Step 2	Step 3	Step 4	Step 5	Step 6
Pb	Temp.(°C)	90	100	130	390	1300	2200
	Ramp (sec)	10	5	5	20	0	0
	Hold (sec)	15	5	10	15	3	3
	Ar flow (mL/ min)	300	300	300	300	0 MP,RD	300 MP

MP: Temperature-Controlled Maximum Power Heating
RD: Read

Wavelength: 283.3 nm
Slit width: 0.7 n m
Lamp current: 10 mA
Background correction: on
Graphite tube: pyrolytically coated
Measurement: peak height
injection volume: 20 µL of sample + 10 µL of modifier $NH_4H_2PO_4$
Standards: 0, 5, 10, 20, 50 $\mu g.L^{-1}$ of Pb in 2% V/V nitric acid

Median concentrations of Cd, Pb, Hg in dustfall are shown in Figures 1. It is evident that median values of all metals in the vicinity of the oil refinery (locality no. 1) were higher than in the other localities.
The Maximum permissible concentrations of metals in agricultural soil in Slovak Republic are 20 $mg.kg^{-1}$, 600 $mg.kg^{-1}$, 10 $mg.kg^{-1}$ for Cd, Pb, Hg, respectively.

Table 3. Results of measured concentrations of metals in SRM

Material	Element	Mean value (µg.g^{-1})	Certified value (µg.g^{-1})
Copper smelting plant flue dust	Cd	416.7 ± 8.0	414.0 - 469.0
	Hg	55.5 ± 3.6	45. 1 - 59.1
Tomato leaves (NBS 1573)	Cd	3. 1 ± 0.4	3 [a]
	Pb	6.51 ± 0.02	6.3 ± 0.3
	Hg	0.11±0.03	0.1[a]
Wheat bread flour	Cd	41.0 ± 2.4	38.3 - 44.7
	Pb	49.5 ± 7.9	33.6 - 49.2
	Hg	3.00 ± 0.53	1.52 3.92

[3]Values are not certified and are listed for information only.

Table 4. Cd, Pb and Hg contents in dustfall (µg.m^{-2}. d^{-1})

Element	Locality									
	1		2		3		4		5	
	min	max	min	max	min	max	min	max	min	max
Cd	0.3	6.13	0.09	2.96	0.03	1.89	0.02	0.77	0.13	0.77
Pb	9	1310	3.3	102.5	1.9	119	0.6	61.9	1.2	42.9
Hg	0.12	0.5	0.08	1.07	0.06	0.45	0.05	0.33	0.04	0.2

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

Table 5. Cd. Pb, Hg contents in air dried soil (µg.kg^{-1})

Element	Locality									
	1		2		3		4		5	
	min	max	min	max	min	max	min	max	min	max
Cd	0.243	0.9	0.15	0.981	0.15	0.883	0.36	1.015	0.366	0.935
Pb	10.06	41.88	8.33	61.14	10.43	51.7	13.48	33.62	24.89	32.1
Hg	0.035	0.14	0.08	0.28	0.056	0.216	0.063	0.313	0.068	0.278

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

These limits are applicable for removal of elements from soil. The natural levels of metals in soil in geological conditions of Slovak territory are 0.8 µg.kg^{-1}, 85 µg.kg^{-1}, 0.3 µg.kg^{-1} for Cd, Pb, Hg, respectively (MP SR 1994).

The contents of the studied metals in air dried soil samples from the localities 1 - 5 are summarized in Table 5. Median contents of Cd, Pb, Hg in air dried soil in the localities under study are shown in Figures 2. The median values in these localities were lower than the parameters given in the official material (MP SR 1994) as natural concentrations.

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 agricultura1 activities. The contents of the metals in vegetables and fruits calculated on dry weight are summarized in Table 6. Median contents of Cd, Pb, Hg in vegetables and fruits are shown in Figures 3. The range (minimum-maximum) of the levels of toxic metals in selected vegetables and fruits calculated on dry weight basis are presented in Table 7. Median contents of Cd, Pb, Hg in selected vegetables and fruits are shown in Figures 4. When comparing the Cd, Pb and Hg contents in various kinds of vegetables and fruits, the lowest values were found in fruits in all localities. Some of the high metal concentrations in the vegetables and fruits correspond to high concentrations of the metals in soil, especially when the locations were near to the source of pollution

Table 6. Cd, Pb, Hg contents in vegetables and fruits ($\mu g.kg^{-1}$d.wt)

Crops	Element	Locality					
		2		3		4	
		min	max	min	max	min	max
Vegetab-les	Cd	0.003	0.2	0.004	0.205	0.008	0.21
	Pb	ND	0.97	ND	0.9	ND	0.7
	Hg	0.001	0.065	0.001	0.046	0.001	0.078
Fruits	Cd	0.001	0.053	0.004	0.01	0.003	0.045
	Pb	ND	0.375	0.02	0.13	ND	0.2
	Hg	0.001	0.017	0.001	0.006	0.001	0.006

2 - Bratislava, 3 - Dunajská Streda, 4 - Pieštany

ND - Not detectable

The median values of the toxic metals found in the crops were used to calculate their daily intakes from the respective vegetables and fruits and compared to the Provisional Tolerable Weekly Intake - PTWI as given by FAO/WHO (Technical Report 1978, 1993), which are 7 µg/kg b.wt. for Cd, 25 µg/kg b.wt for Pb and 5 µg/kg b.wt. for Hg.

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.

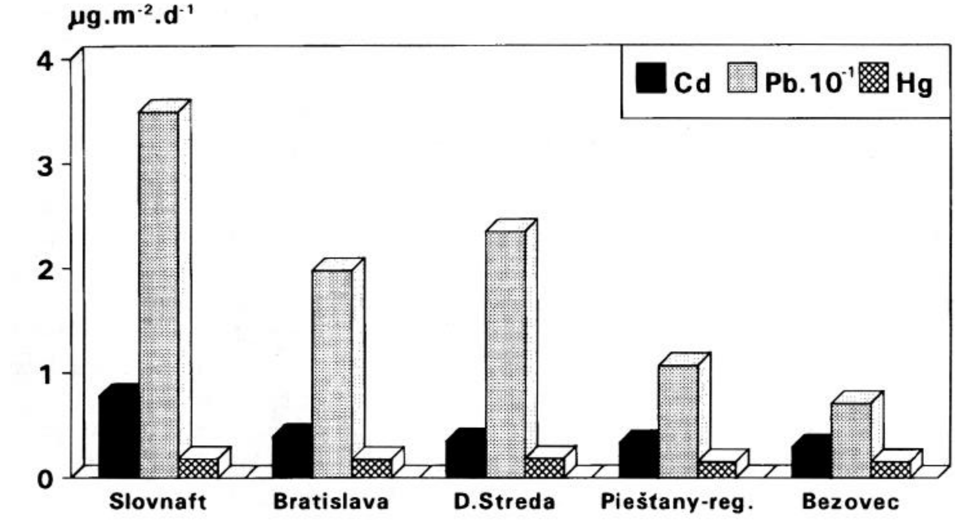

Figure 1. Median Cd, Pb and Hg concentrations in dustfall

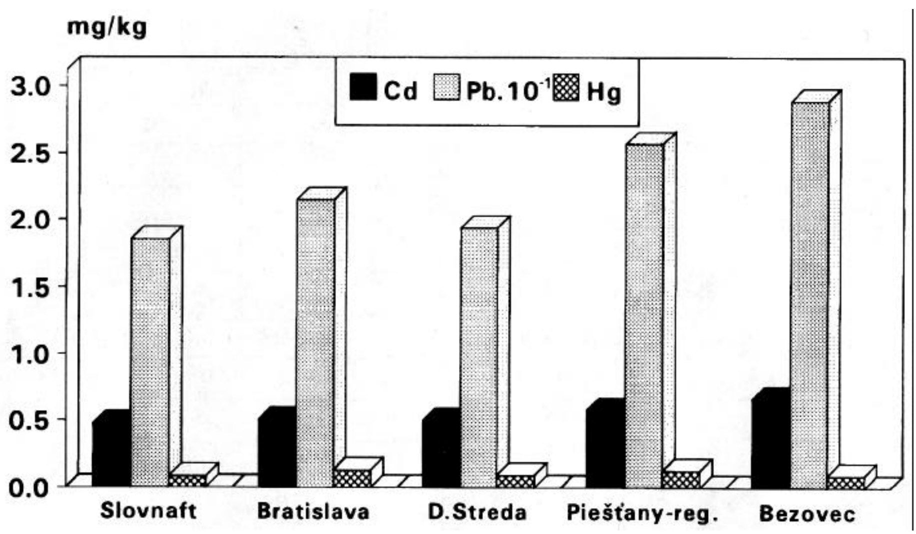

Figure 2. Median Cd, Pb and Hg concentrations in air dried soil

According to our calculations and on the basis of the metal contents found in crops the daily intakes of Cd, Pb and Hg from vegetables amounted to 3.52 µg Cd, 11.09 µg Pb and 0.85 µg Hg for an average person. After recalculation to weekly intakes per kg b.wt.(mean body weight of adults = 64 kg), a comparison with the respective PTWI values shows that vegetable consumption is responsible for 5.4 % PTWI of Cd, 4.8 % PTWI of Pb and 1.8 % PTWI of Hg in average adult from the regions studied.

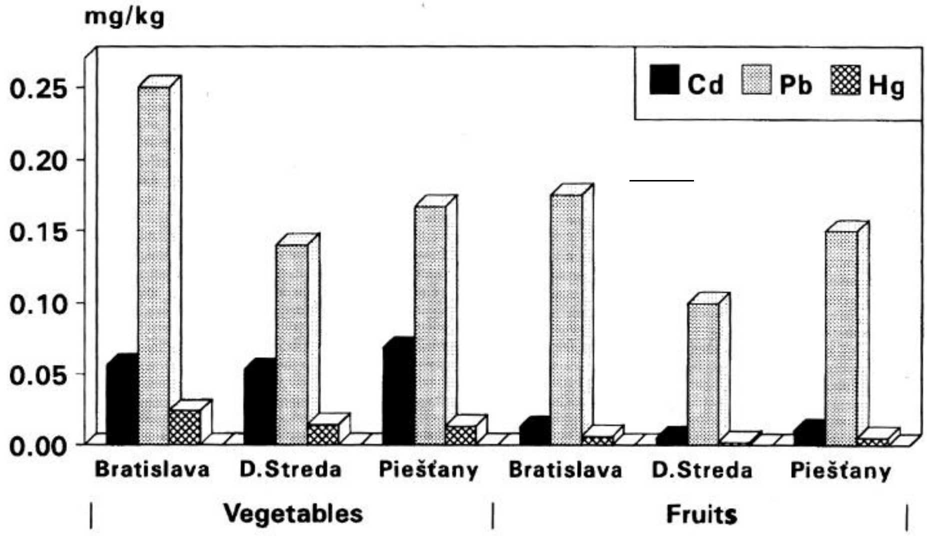

Figure 3. Median Cd, Pb and Hg concentrations in vegetables and fruits

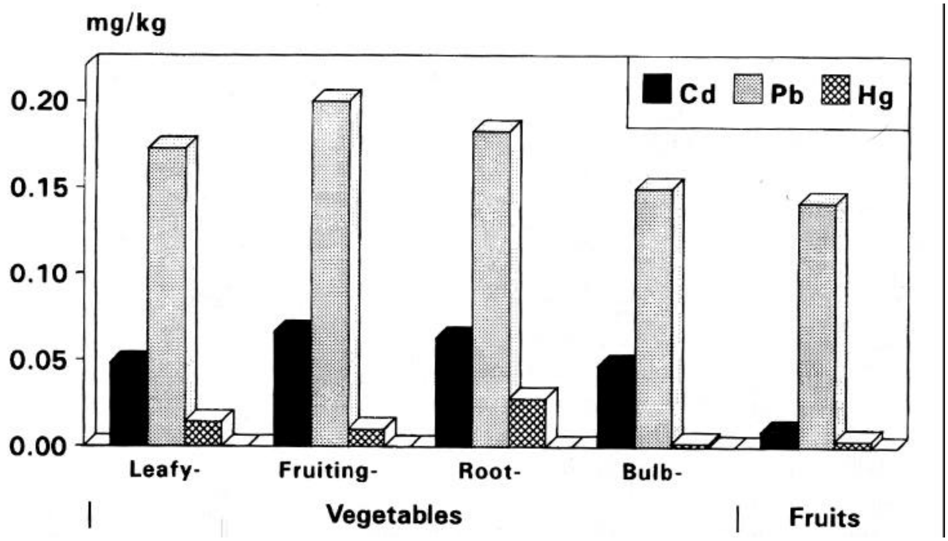

Figure 4. Median Cd, Pb and Hg concentrations in selected vegetables and fruits

The daily intakes of Cd, Pb and Hg from fruits were 0.28 µg Cd, 4.46 µg Pb, 0.13 µg Hg for average person. This represents 0.4 % Cd, 1.9 % Pb and 0.3 % Hg of the respective PTWI values.

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, the values might be slightly influenced by the consumption of imported crops where contents of the respective metals may be slightly different.

Table 7. Cd, Pb, Hg contents in vegetables and fruits (µg.kg^{-1} d.wt.)

Vegetables	Cd		Pb		Hg	
	min	max	min	max	min	max
Leafy-	4	205	ND	900	1	78
Fruting-	3	200	ND	970	1	28
Root-	14	210	ND	500	1	65
Bulb-	20	111	ND	375	1	18
Fuits	1	53	ND	375	1	17

ND - Not detectable

However, even considering the concentrations of the toxic metals in industrial regions which are higher than those in unexposed regions, the results of this study in comparison with PTWI values indicate that the intakes of Cd, Pb and Hg through vegetables and fruits from Slovakia would not mean a health hazard for consumers.

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