Soil and plant pollution by potentially toxic elements in Slovakia

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ABSTRACT

The Problem of soil and plant pollution by heavy metals in Slovakia is evaluated in this study. The measured data on the main risk elements have been obtained from a soil-monitoring grid in Slovakia, which consists of 318 agricultural sites. Analytical procedures of Cd, Pb, Cr, Ni, Zn, Cu (extracted by 2 mol/l HNO_3 and by 0.05 mol/l EDTA) as well as the total content of the described elements including Hg have been used for soil samples. Also the plants collected at the same sampling sites were analysed for their Cd, Pb, Cr and Hg contents. On the basis of the obtained results it may be concluded that significant pollution was determined only on 0.4% of the total soil cover in Slovakia. The significant correlation was determined between the soil available heavy metal content (extracted by 0.05 mol/l EDTA) and plant content. Potentially toxic elements were accumulated in the plant biomass only on heavily polluted soils.

Keywords: heavy metal; soil; plant; environment; monitoring

Slovakia has been characterised by frequent and extensive changes unfavourably impacting all aspects of the environment especially during the second half of last century. Long-term continuing wasteful exploitation of natural resources, extensive pollution of the air, water, soil and land, release of pollutants into the environment is often very significant. In addition, the occurrence of natural endogenous geochemical anomalies are particularly prevalent in the Western Carpathians including Slovakia. Geochemical anomalies occur especially on volcanic and crystalline rocks in mountainous regions where it is possible to measure high contents of risk elements (Cd, Pb, Cu, Zn, Hg).

Generally, it can be summarized that soil pollution can be caused by:
– the anthropogenic influence (industry, agriculture, municipal waste material, etc.)
– the geogenic influence (occurrence of geochemical anomalies)
– the mixed influence, where the content of risk elements is often extremely high

All described areas with various influences are included in this work. Heavy metals, which are deposited from the atmosphere, are bound in more easily extractable forms than those of geological origin (Chlopecka et al. 1996, Wilcke and Kaupenjohann 1997). Therefore, a non-exhaustive extractant like ethylenediaminetetraacetic acid (EDTA) at pH 4.6 may be used to characterise anthropogenic inputs of elements. Moreover, EDTA-extractable metal contents reasonably determined in a broad range of soils (Hornburg and Brümmer 1993). In addition, it was found that the concentration of elements extracted by 0.05 mol/l EDTA is often not in relation to their concentration measured as total content (by the use of HCl + HNO_3 + HF acids) or extracted by 2 mol/l HNO_3. Therefore the use of 0.05 mol/l EDTA extractant is more suitable for the evaluation of soil-plant transport of elements instead of the application of strong acid extractants (Kobza 2003).

The pollution of the soil causes a lot of negative effects. One of them is transport of toxic elements to the plants. For this reason, many studies were focused on empirical models (Gupta and Aten 1993, Dudka et al. 1996). The relationship between metal concentrations in soils and plants is often described with a transfer function, which is usually determined by regression analysis. Linear equations are preferred in most cases (Smilde et al. 1992, Miner and King 1997). In addition, Langmuir and Freundlich equations are often used for predicting heavy metal transfer from soil to plant (Krauss et al. 2002).

MATERIAL AND METHODS

All the topsoil of the country has been analysed by the use of a soil monitoring network (Figure 1). The soil-monitoring network was constructed on the basis of ecological principles including all soil types and subtypes, climatic regions, emission re-

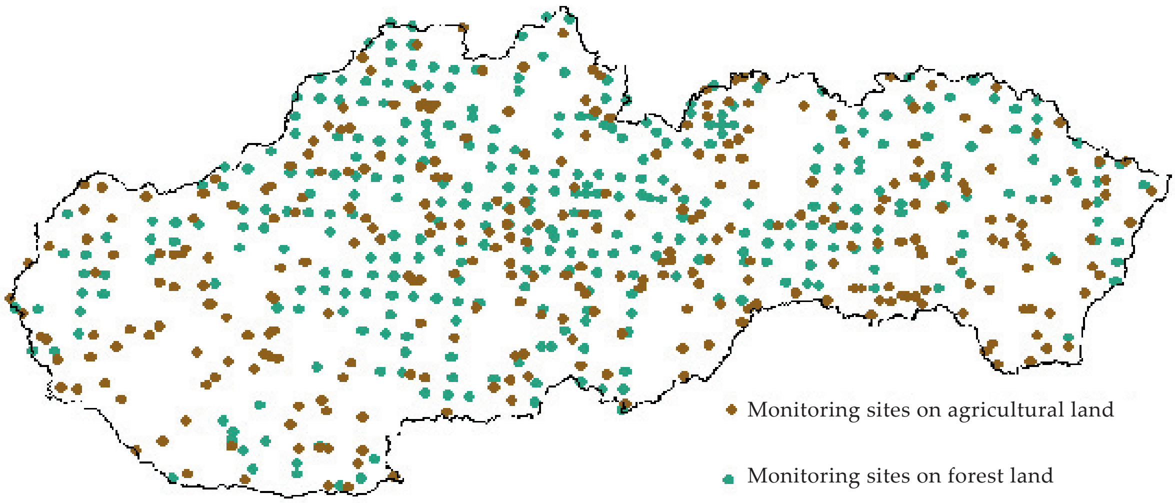

Figure 1. Soil monitoring network in Slovakia

gions, relatively clear regions, highland as well as the areas with natural geochemical anomaly occurrences in Slovakia.

The soil-monitoring network consists of 429 monitoring sites in total. 318 monitoring sites were selected from agricultural land and 112 monitoring sites from forestland. Soil samples for heavy metal determination were collected from the surface layer (depth 0–10 cm) together with the plant samples. The heavy metal contents in the soils (Pb, Cd, Cr, Cu, Ni, Zn) were determined in extracts by 2 mol/l HNO_3 (2 hours extraction) and by 0.05 mol/l EDTA (1 hour extraction). For the determination of the total mercury in the soils, a single-purpose mercury analyser TMA 254 was applied. Besides the extractable values, soils were analysed for their total content of heavy metals (Cd, Pb, Cr, Ni, Cu, Zn) extracted by mixture of acids (HCl + HNO_3 + HF) with respect to related total content of heavy metals in plants. All analytical methods are described in more detail in the paper written by Fiala et al. (1999). The analyses were performed in the certified laboratory at Soil Science and Conservation Research Institute in Bratislava. The obtained results were evaluated by a basic statistical program (Statgraphic 5.0) and presented in numerical, tabular and graphical outputs in GIS presentation.

RESULTS AND DISCUSSION

The distribution of heavy metals in agricultural soils of Slovakia is presented in Table 1.

High concentrations of cadmium (Cd) were found at geochemical anomalies. The cadmium from phosphorus fertilisers did not have any clear effects on the pollution of the soils. The influence of P-fertilization is very low and only evident after a long-term period (50 and more years).

Table 1. The results of heavy metal determinations in agricultural soils of Slovakia (mg/kg)

Heavy metals	Total content			Content in 2 mol/l HNO_3				Content in 0.05 mol/l EDTA			
	X_G	min	max	X_G	min	max	% total content	X_G	min	max	% total content
Cd	0.285	0.050	9.05	0.169	0.010	6.85	59.3	0.088	0.010	3.60	30.9
Pb	24.9	9.5	1050	14.2	3.70	649	57.2	3.56	0.160	268	14.3
Cr	72.7	10.5	170	2.09	0.100	43.1	2.87	0.162	0.010	2.90	0.220
Ni	12.8	0.3	57.5	3.22	0.200	19.1	25.1	1.04	0.110	8.60	8.12
Cu	22.3	5.0	156	7.55	1.00	171	33.4	3.27	0.300	80.5	14.5
Zn	64.3	11.0	1070	12.3	2.05	565	19.2	2.35	0.050	126	3.66
Hg	0.075	0.009	6.69	–	–	–	–	–	–	–	–

X_G – geometric mean, min – minimum value, max – maximum value

High values of lead (Pb) were determined especially in areas with geochemical anomalies, mostly in the mountainous regions. The lead, originating from the traffic along the highways, had no significant effects on soil pollution. The effect of traffic on the soil lead pollution was about 2–7 mg Pb/kg and this range did not exceed the critical values of pollution.

High values of chromium (Cr) were determined especially in Dolna Orava region and in northern part of Slovakia as a result of metallurgy activities in Istebne, partly from Poland (Linkeš et al. 1997).

Increased values of nickel (Ni) could probably be caused by the influence of emissions, and partly by the influence of geochemical anomalies especially in the Strážovské Vrchy and Malá Fatra mountains. The highest values occurred in the mountainous regions.

The highest values of mercury (Hg) were determined in Central Spiš region at the Eastern Slovakia where both anthropogenic and geogenic influences coexisted.

Copper (Cu) frequently occurs especially in old mining areas in Slovakia. Extremely high values were determined in Central Spiš region of Eastern Slovakia. In these areas soil Cu contents were found higher than 100–150 mg/kg.

Zinc (Zn) occurs in association with copper. The highest values occurred in areas with geochemical anomaly influence at Štiavnicke Vrchy Mountains and Central Spiš region. High values of zinc were also determined in some alluvial deposits as a result of inundation activity of some rivers.

The Cd, Pb, Ni contents of forestland was relatively higher than in agricultural land. This was due to the occurrence of geochemical anomalies in mountainous regions, where the maximum values of heavy metals have been measured. The results of heavy metal measurements varied according to the type of extraction method. When the values obtained by total and 2 mol/l HNO_3 extraction method are compared there was no distinction in the heavy metal content of agricultural and forest lands, except for nickel. Nickel contents of the agricultural land are influenced by nickel metallurgy in farming land. This reveals that the total nickel content of the rocks is quite low. Available and mobile forms of heavy metals determined by the 0.05 mol/l EDTA extraction method are more dynamic and variable. 0.05 mol/l EDTA extraction method gives more realistic results for assessing heavy metal contents of the soils in areas where anthropogenic influence is dominant and especially for Cd, Pb and Cu contents of the soil. The graphical presentation of the present soil pollution status is given in the map (Figure 2), calculated as arithmetic mean of all elements content, and relative distribution of the soil pollution categories is illustrated by Figure 3.

Heavy metal limits (total content) for Slovakia (MPSR 1994)

1. Less than A value: **non-polluted soils** (A values for elements in mg/kg: Cd – 0.8, Cr – 130, Cu – 36, Ni – 35, Pb – 85, Zn – 140, Hg – 0.3)
2. Between A–B values: **non-polluted soils** (only increased background values; B values for elements in mg/kg: Cd – 5, Cr – 250, Cu – 100, Ni – 100, Pb – 150, Zn – 500, Hg – 2)

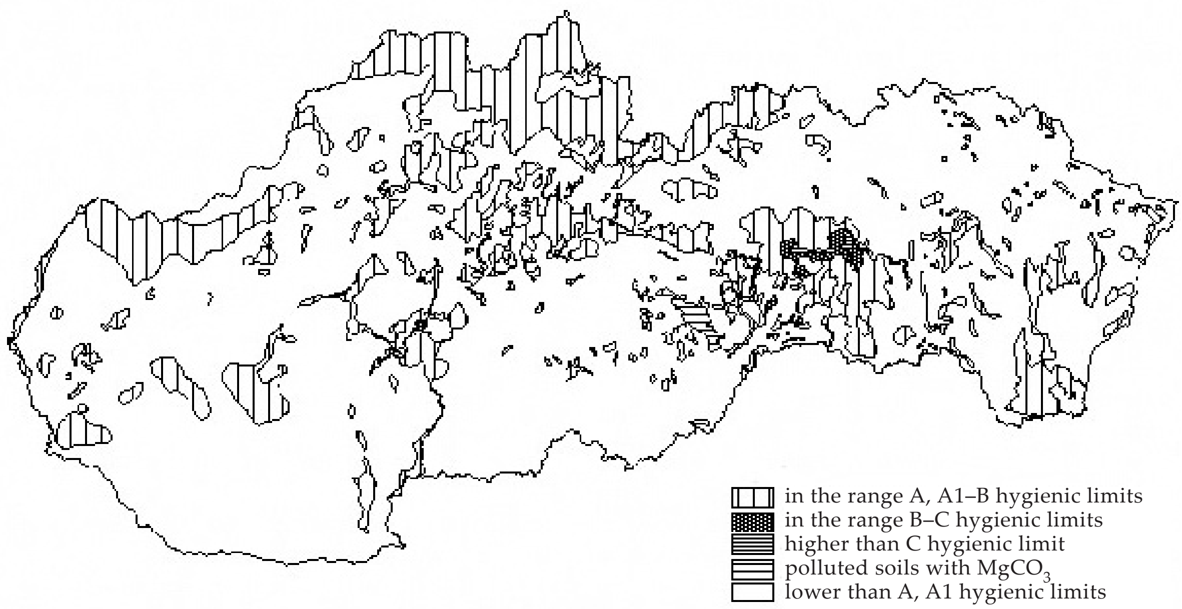

Figure 2. Soil pollution categories in Slovakia

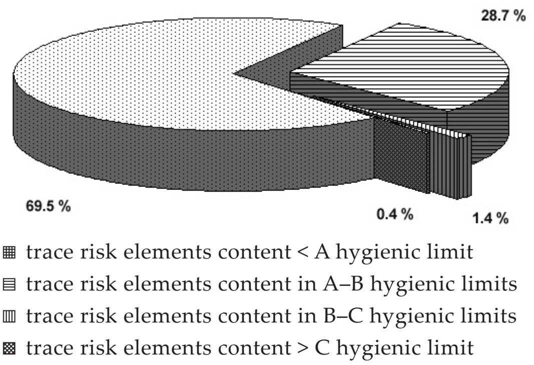

Figure 3. Distribution of the soil pollution categories in Slovakia

3. Between B–C values**: polluted soils** (C values for elements in mg/kg: Cd – 20, Cr – 800, Cu – 500, Ni – 500, Pb – 600, Zn – 3000, Hg – 10)
4. Higher than C value: **extremely polluted soils** (remediation of soils is necessary)

Extent of soil pollution in Slovakia

The areas with non-polluted soils are widespread in the south and southwestern parts of Slovakia where fertile soils take place. All toxic element contents were below limit A (for total content). Areas with non-polluted soils lay in the range A–B limits (increased background values). Those areas are especially widespread in the northern part of Slovakia as the result of long-term anthropogenic influence. Part of the anthropogenic effect is from abroad. Those areas are in the central and eastern part of Slovakia where at least one of the toxic elements overlaps limit A up to limit B.

The areas with polluted soils are in the range B–C limits and can be described as ones with clearly negative impact on population and environment. These areas are widespread mainly in Slovenské Rudohorie Mountains – in Central Spiš region at eastern Slovakia where the influence of anthropogenic factors (industry) and geochemical anomalies are combined resulting in a high concentration of potentially toxic trace elements such as Hg, Cu and Zn. At least the level of one of the risk substances overlaps limit B up to the limit C of the legislative regulation. At these soils, an increased content of risk substances in plant, above permitted limits for food can be demonstrated in the majority of cases.

Areas with extremely polluted soils (higher than C hygienic limit)

These areas are also widespread in Central Spiš region (eastern Slovakia) where the anthropogenic and geogenic factors are combined. At least the level of one of the risk substances overlaps the C limit and this is demonstrated in its high content in plants, so that legislative standard determines these soils should be rehabilitated and the entrance of potentially contaminated plants into the food chain is closely controlled. There are about 15 000 ha of these polluted soils in Slovakia (category higher than C hygienic limit).

Heavy metals in plants, transfer from soil and phytotoxicity

Pollution causes many negative effects on soil quality. One of these effects is intake of the most important pollutants into the food chain and environment. The transfer of soil pollutants into the plants causes many physiological disorders. Plant uptake of pollutants from the soil is determined by pollutants distribution in the soil (Passdar 1994), by the intensity and specificity of plant physiological processes (Young 1992) and by the soil properties regulating the vulnerability of different soils to different pollutants.

PH values, organic matter quality and quantity, redox potential, clay content, manuring, and plant species determine heavy metal availability and plant uptake. Bioavailability of heavy metals is accelerated by a decrease of pH value; humus and clay content (Kobza et al. 2003). A high plant uptake is reflected in a decrease of biomass quantity and quality. Pollutants are accumulated in the plant biomass (Table 2). Also the development of generative organs is restricted.

Table 2. Contents of risk elements in plants (arithmetic mean)

Plant	Cd	Pb	Cr	Hg
	mg/kg of dry matter			
Pasture	0.27	1.80	1.35	0.06
Meadow	0.12	0.85	2.70	0.03
Clover	0.09	1.40	1.29	0.02
Lucerne	0.11	1.32	1.14	0.23
Silage maize	0.15	12.2	4.61	1.29
Grain maize	0.14	1.08	2.87	0.02
Pea	0.06	1.04	0.95	0.02
Oat	0.70	4.40	1.39	0.02
Ray	0.20	0.68	2.56	0.05
Spring barley	0.12	2.96	2.43	0.04
Winter wheat	0.12	1.43	3.62	0.06

Table 3. Correlation between Cd contents in soil and plant

Cd in soil	Cd in plants	Correlation coefficient
Total content	total content	0.17
Content in 2 mol/l HNO_3	total content	0.44
Content in 0.05 mol/l EDTA	total content	0.77

Table 4. Normal and phytotoxic contents of heavy metals in grass (Beneš 1994) and their highest admissible amounts in feeds (MPVžSR 1984)

Heavy metals	Normal content (mg/kg)	Phytotoxic content (mg/kg) with crop decrease about 50%	The highest admissible amount in feeds (mg/kg)
Cd	0–2.0	> 100.0	0.2
Pb	2.0–14.0	> 60.0	10.0
Zn	25.0–150.0	> 400.0	250.0
Cu	6.0–15.0	> 20.0	50.0

Plant uptake of heavy metals partly correlates with the total content of heavy metals in the soils. But a higher coefficient of correlation (*r*) was found between the 2 mol/l HNO_3 extracted amounts soil heavy metal content and plant content whereas the highest coefficient of correlation (*r*) was between the 0.05 mol/l EDTA extracted soil amounts and plant contents. Correlations between the soil and plant Cd contents are presented in Table 3.

The transfer of heavy metals from soil to plant is important with regard to plant nutrition (Marschner 1995) and the pollution of crops by heavy metals (McBride 1995). Soil-plant transfer of metals often is described with curvilinear functions determined by regression analysis. In the framework of our common long-term cooperation with the University of Bayreuth (Krauss et al. 2002) we have tried to use the potential of Freundlich ($c_{plant} = b.c_{soil}{}^{a}$) and Langmuir [$c_{plant} = a.c_{soil}/(b + c_{soil})$] equations to predict Cd, Cu, Pb and Zn concentrations in wheat (*Triticum aestivum* L.) grain and leaf from soil concentrations. At 34 agricultural sites in Slovakia, wheat plants and horizons from mainly alluvial soils were sampled. The relationships between soil and grain content of heavy metals (Zn, Cu, Cd and Pb) in the field modelled with the Freundlich equation are illustrated schematically in Figure 4, which indicates that content in grain decline at a given soil content along the line Zn > Cu > Cd > Pb.

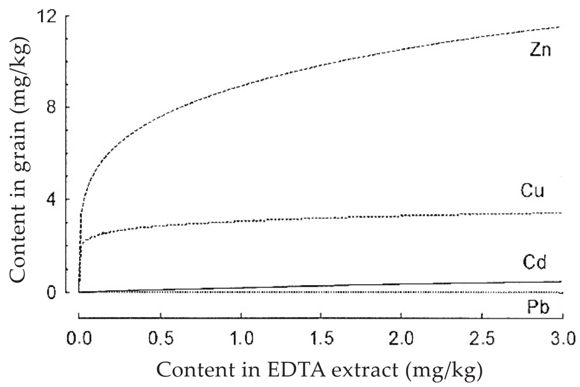

Figure 4. Potential of Freundlich and Langmuir equations for individual elements

Concerning content of heavy metals in soils and plants the problem of phytotoxicity is discussed worldwide. In the following Table 4, the normal and phytotoxic contents of heavy metals in grass are given (Beneš 1994). Also the highest admissible amount of heavy metals in the feeds is described in Table 4 (MPVžSR 1984).

On the basis of obtained results it may be concluded that the phytotoxic content of heavy metals in plants according to previous criteria has not been exceeded in conditions of Slovakia. Only the highest admissible amount of Cd in feeds in some cases was more or less exceeded mostly in permanent grass in regions with geochemical anomalies occurrence (above all mountainous regions with polymetallic ore mineralisation).

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ABSTRAKT

Kontaminace půdy a rostlin na Slovensku rizikovými prvky

Příspěvek hodnotí kontaminaci půd a rostlin toxickými prvky na celém území Slovenska. Z půdní monitorovací sítě, která sestává z 318 odběrových míst na zemědělských půdách, byla získána analytická data obsahu hlavních rizikových prvků (Cd, Pb, Cr, Ni, Zn, Cu) v půdách. Prvky byly stanoveny v extraktech půdních vzorků 2 mol/l HNO_3 a 0,05 mol/l EDTA. Zároveň byly stanoveny i celkové obsahy prvků v půdách včetně rtuti. Celkový obsah vybraných rizikových prvků (Cd, Pb, Cr, Hg) byl stanoven i v rostlinách odebraných na stejných odběrových místech. Na základě získaných výsledků lze konstatovat, že významná kontaminace půd (převyšující limit C) byla zaznamenána pouze na výměře 0,4 % půdního krytu Slovenska. Pouze u půdního výluhu 0.05 mol/l EDTA byla zaznamenána významná korelace mezi extrahovatelnými obsahy prvků a obsahem těchto prvků v rostlinách. Významná kumulace sledovaných prvků v rostlinách byla zaznamenána pouze na nejznečištěnějších půdách.

Klíčová slova: těžké kovy; půda; rostlina; životní prostředí; monitoring

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