THRESHOLD LIMIT VALUES FOR HEAVY METALS IN SOILS IN THE FUNCTION OF SPATIAL AND TEMPORAL VARIATION OF GEOCHEMICAL FACTORS

P. SIPOS and T. PÓKA

Laboratory for Geochemical Research, Hungarian Academy of Sciences, H-1112 Budapest, Budaörsi út 45., Hungary; sipos@geochem.hu

Abstract: The following respects must be taken into account at the determination of threshold limit values (TLV) in soils: the spatial and temporal changes of geochemical background, the possible effect of deep geological structures, natural anomalies exceeding the TLV by order of magnitudes, and the results of monitoring examination of element (groups). In addition, the TLV of given country must be legitimated according to the co-ordinated experiences of different environmental scientific teams.

Key words: environmental geochemistry, heavy metals, soils, geochemical background, threshold limit values (TLV), geochemical factors

Introduction

To assess and apply the threshold limit values (TLV) we need to know the average and concrete geochemical background values as well as their possible spatial and temporal variation and we need to prognosticate this variation. Hereinafter, this question is examined on the grounds of regional and applied environmental geochemical researches running at the Laboratory for Geochemical Research.

TLV (B value) defined by the Hungarian governmental regulation (number 10/2000) are too close to the average concentration of certain elements in soils in Hungary (Table 1.). On the other hand, natural processes may lead to anomalies exceeding the B values by order of magnitude without any anthropogenic contamination.

	Average concentrations in soil [a, b, c]	B value (threshold limit value) [d]	Extent of anomalies of natural origin [a, b, c]	Maximal available amount in the percentage of total concentration [c]
Cr	50-200	75	3500	5
Co	10-15	30	300	30
Ni	15-30	40	5000	20
Cu	15-40	75	250	20
Zn	50-100	200	900	20
As	0,1-15	15	No data	38
Se	0,1-3	1	120	7
Mo	1-2	7	101	27
Cd	0,01-2	1	No data	20
Sn	1-5	30	50	No data
Ba	100-500	250	3000	No data
Hg	0,01-5	0,5	No data	11
Pb	15-30	100	1200	12
Ag	1-2	2	30	No data

Table 1.: Trace metal contents of soils. References: a) Aubert and Pinta (1978); b) Kabata-Pendias and Pendias (1984); c) Adriano (1986); d) Hungarian Governmental regulation number 10/2000 (2000).

Factors forming the natural geochemical background

The mineralogical and geochemical characteristics of soil parent material determinate the similar characteristics of soil developed from it. The bedrock is the primary source of chemical elements in soils. The clay mineralogy of soils characterized by similar pedogenic processes shows large variations on different parent materials according to the environmental studies at the Cserhát Mts., North Hungary. (Sipos and Németh, 2001; Figure 1.).

The type of weathering and pedogenic processes (clay migration, gley formation, podzolization, etc.) determine the quality of phases formed in soils, hereby they also have effect on the behaviour of trace metals in soils (Palumbo et al., 2000). Not only the soil type, but the soil horizons formed by the effect of pedogenic processes determine the retardation of heavy metals in soils (de Matos et al., 2001).

The mineralogical and grain size composition of soil and their variation also have effect on the behaviour of chemical elements in soils. The organic matter, clay minerals and amorphous Fe, Mn and Al oxides have the main role in the adsorption of trace metals. This chemical elements accumulate in the clay fraction of soils (Table 2.), while the phases listed above enrich in this fraction.

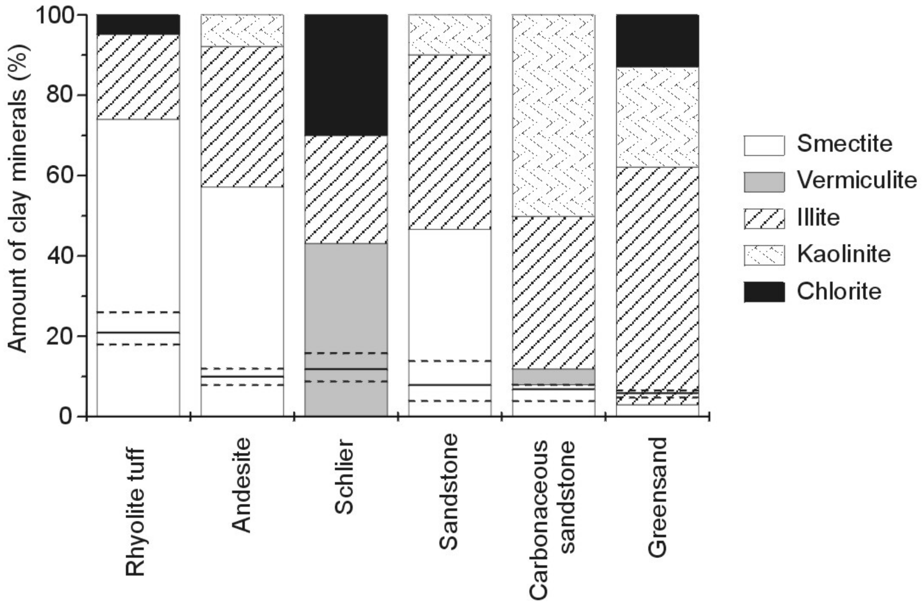

Figure 1.: Proportion of clay minerals in the clay fractions of Luvisols derived from different parent material.

	Rhyolite tuff	Andesite	Schlier	Sandstone	Carb. sandstone	Greensand	Average
Co	1.70	0.83	1.86	2.42	1.79	2.23	1.81
Ni	1.16	0.94	1.25	1.36	1.03	1.33	1.18
Cu	1.16	0.85	1.16	1.06	1.03	0.90	1.03
Zn	1.52	0.83	1.56	1.99	1.51	2.06	1.58

Table 2.: Accumulation of trace metals in clay fraction of Luvisols derived from different parent material (Sipos and Németh, 2001).

There is an obvious relationship between the clay mineral content and the amount of trace metals in soils (Figure 2.), which is strongly influenced by the quality of soil clay minerals. Generally, the same clay mineral assemblage appears in a given soil profile, but the proportion of different clay mineral species and mixed layer phases may vary with the depth. The clay fraction of different soil types is characterized by the predominance of mixed layer clay mineral phases, which can affect the adsorption capacity of soils (Figure 3.).

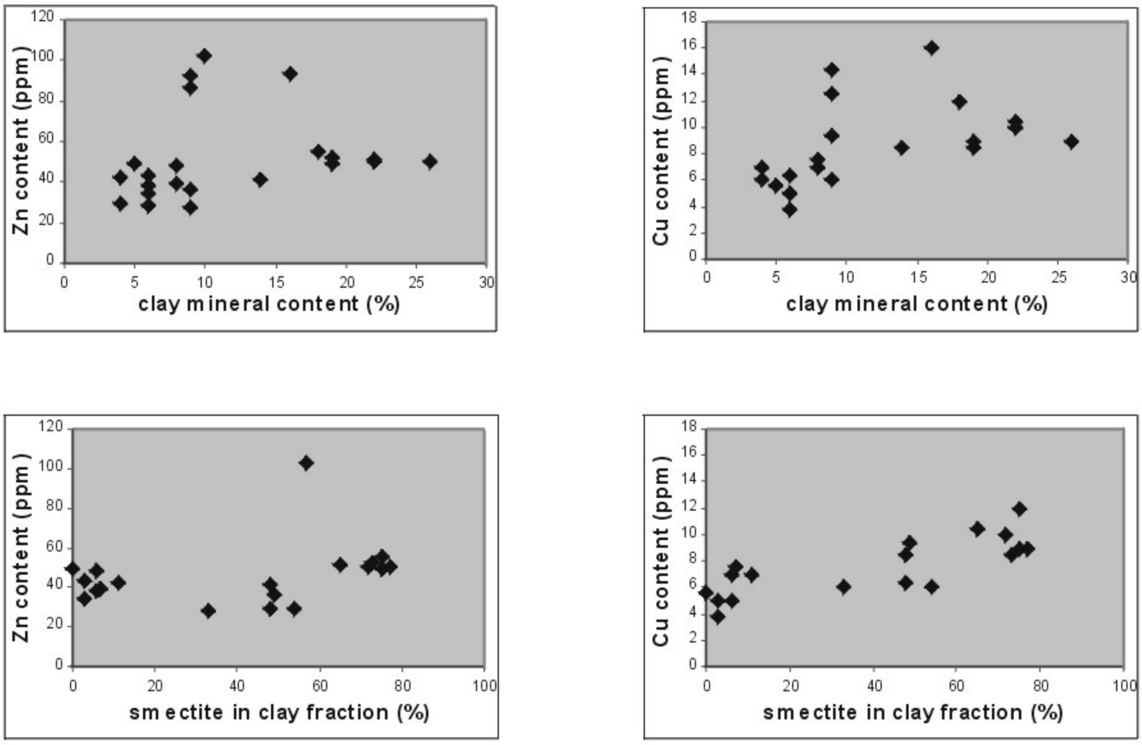

Figure 2.: Relationship between clay mineralogy and heavy metal content of soils.

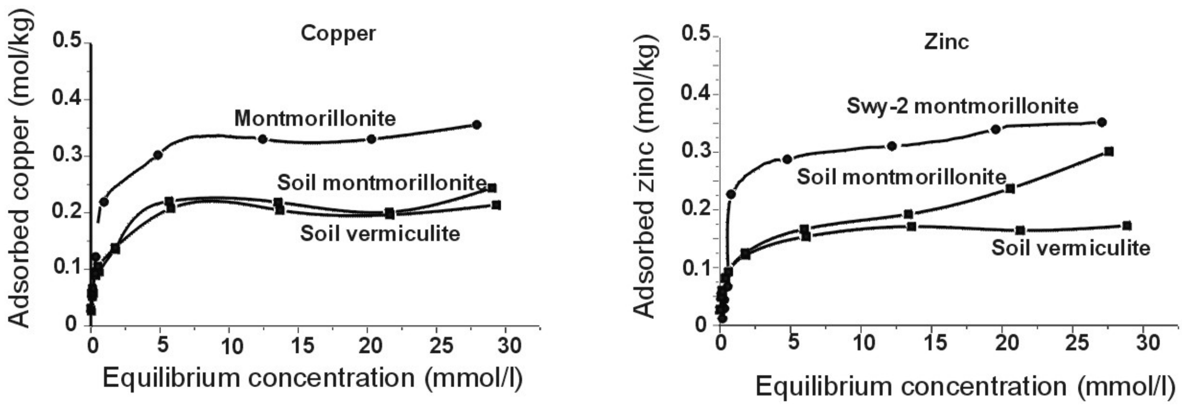

Figure 3.: Adsorption of copper and zinc on different soil clays.

Environmental changes affecting the geochemical background

The weathering and pedogenic processes are active in the course of pedogenesis, so they play a role not only in the forming of background, but in its continuous development, as well.

The plant uptake and the natural washing out lower the trace metal content of soils. The output of trace metals may exceed the input only in extreme case.

The climate is an important factor affecting intensity of the weathering and pedogenic processes. The periodic and catastrophic seasonal changes, the long scale changes of climate affect the factors determining the distribution of chemical elements. 500-600 mm annual precipitation has no effect on behaviour of trace elements in soils, but above1000 mm/year the depletion and enrichment trends are observable well (Teutsch et al., 1999). The continuous drying-wetting cycles influence the speciation of heavy metals in soils in short-term period (Han et al., 2001).

The deep flow systems driving the subsurface fluids (water, oil, gas) also have an effect on the surface, which is perceptible in the distribution of trace metals. A reductive cell generates above the hydrocarbon deposits, which results in migration of chemical elements on the surface. The reductive sensitive metals (Fe, U, Th, Ca, S, I, K, Ni, Cu and Zn) enrich at the boundary of reductive cell and the surrounding oxidative area (Tompkins, 1990; Figure 4.). This process has an important role in the developing of distribution of chemical elements on the surface in Hungary. In the surroundings of hydrocarbon deposits there were established trace element accumulation (Table 3.) and radon anomalies too.

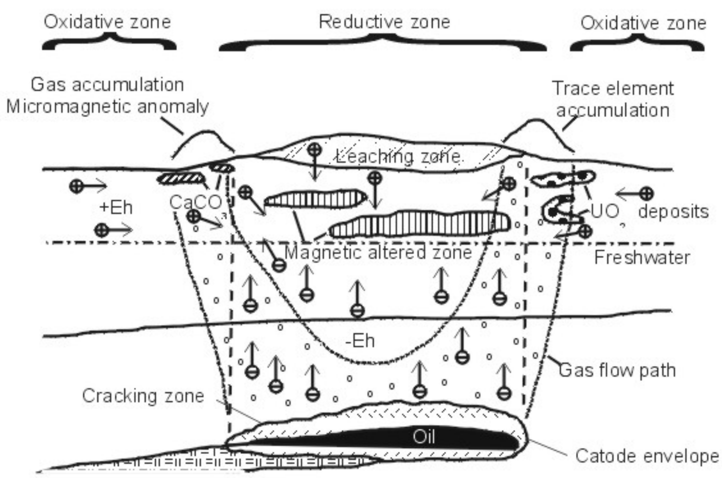

Figure 4.: the reductive cell forming above hydrocarbon deposits and its effect on trace metal distribution on the surface after Tompkins (1990).

Discussion

Significant spatial (vertical and horizontal) and temporal inhomogenities can form in the geochemical background due to the effect of factors listed above. The most of effects do not mean direct chemical element input, but they act on the geochemical factors (pH, Eh) affecting the behaviour of chemical elements in soils indirectly. The examination of individual chemical elements or element groups is very important, because the different chemical elements behave distinctly by the pH and Eh changes.

The heavy metals can accumulate or deplete, the available amount of metals can change, as well as the soil reacts to the contamination distinctly through the effect of geological and geochemical processes mentioned above.

Area and soil type		Co	Ni	Zn	Cu
Duna-Tisza area, Regosols	Average	200	104	124,4	47,3
	Min-max	(7-700)	(4-400)	(60-360)	(5-85)
Hatvani plain, Chernozems	Average	11,6	20,3	84,3	21,4
	Min-max	(5-43)	(3-70)	(0-150)	(5-46)
Dráva valley, Luvisols	Average	10,8	10,8	70,3	9,8
	Min-max	(5-18)	(5-18)	(30-120)	(3-15)
Kis-Balaton, Histosols	Average	150,2	120,2	104	43,7
	Min-max	(5-400)	(4-450)	(50-170)	(7-350)

Table 3.: Changes of heavy metal content in soils above some hydrocarbon deposits in Hungary (in ppm).

Conclusions

- The spatial and temporal changes of geochemical background must be considered by the determination of TLV of a country.
- The monitoring examination of chemical elements or element groups is expedient at the determination of differentiated TLV of individual areas.
- Anomalies exceeding the TLV by order of magnitudes can form by geological processes.
- The possible effect of deep geological structures must be considered by the determination of TLV, as well.
- The TLV of given country must be legitimated according to the co-ordinated experiences of different environmental scientific teams.

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