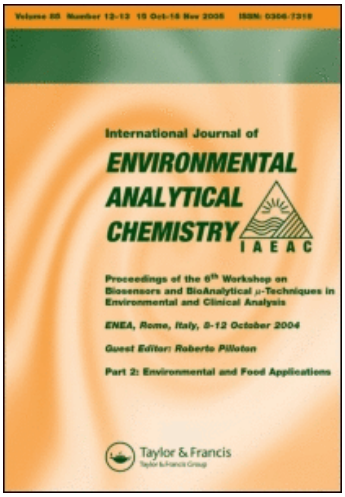


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Some Aspects of the Mobility and Distribution of Toxic Heavy Metal Contaminants Insoil Profiles and River Sediments

L. Hargitai[a]
[a] Department of Soil Science and Agrochemistry, University of Horticulture and Food Industry, Budapest, Hungary

To cite this Article Hargitai, L.(1995) 'Some Aspects of the Mobility and Distribution of Toxic Heavy Metal Contaminants Insoil Profiles and River Sediments', International Journal of Environmental Analytical Chemistry, 59: 2, 317 — 325
To link to this Article: DOI: 10.1080/03067319508041337
URL: http://dx.doi.org/10.1080/03067319508041337

Intern. J. Environ. Anal. Chem., Vol. 59, pp. 317–325
Reprints available directly from the publisher
Photocopying permitted by license only

SOME ASPECTS OF THE MOBILITY AND DISTRIBUTION OF TOXIC HEAVY METAL CONTAMINANTS IN SOIL PROFILES AND RIVER SEDIMENTS

L. HARGITAI

Department of Soil Science and Agrochemistry , University of Horticulture and Food Industry Villányi ut 35–43, H-1118 Budapest, Hungary

(Received, 11 August 1993; in final form, 20 September 1994)

Investigations of the distribution and mobility of Pb, Ni, Cd and Hg have shown that Pb is strongly associated with humic substances in the top layer of soils and in river sediments, and that Pb shows the highest organophilicity. Ni is very organophilic, and Cd, somewhat less so. The hydrophilicity of Hg highly influences its movement in soil profiles and river sediments. The risk of contamination by these metals is characterized through the environment protection capacity (EPC_G) values which combine humus content and the quality and thickness of the humus layer in one parameter. The risk of contamination is highest at low EPC_G values. Increase of EPC_G decreases the risk of environmental contamination through binding of heavy metals to humic substances, decreasing their mobility.

KEY WORDS: Soil and sediment contamination, heavy metals, organophilicity, hydrophilicity.

INTRODUCTION

Investigations of environmental contamination in major Hungarian Industrial Districts focused initially on the distribution and mobility of the most toxic metals, Pb, Ni, Cd, Cr and Hg. Fundamental results on the emission and distribution of toxic heavy metals in the environment were considered. There are two main sources: natural and anthropogenic. Anthropogenic input of Pb is very high[1]; the annual input of toxic heavy metals to the environment compared to their natural concentrations in unpolluted sediments, soils, and waters can be expressed as their technophilicity index[2]. For a number of heavy metals, the technophilicity indices in increasing order are as follows[3]:

Mn		Fe		Ni		Cr		Zn		Cu		Ag		Hg		Pb		Au		Cd
	=		<		<		<		<		=		<		=		<		<	
1		1		2		4		10		20		20		30		30		60		140

The current work investigates the binding and mobility of the toxic heavy metals in soils and sediments. Industrial (anthropogenic) contaminants such as Pb, Cd, and Hg are the most dangerous[4]. Cr and Ni contamination may also be important in special cases, but their concentrations and occurrence are expected to be much smaller.

Current investigations were based on long term model experiments using sewage sludge treatments on brown forest soils[5]. The mobility of toxic heavy metals added to the soils was investigated with rates of sewage sludge application from 50 mm/ha to 1200 mm/ha over a period of 10 y. The increase of organic matter content in soils

depressed the mobile concentration of mobile heavy metals compared to those in the applied sewage sludge. The extent to which the mobile concentration was affected varied among the four metals in that study. The theoretical increase in the mobile concentration of heavy metals, assuming no retention by organic matter, was 24 × ambient concentration for the highest sludge application rate. For Ni, the measured concentration was only 4.06 times ambient: for Pb, 5.75; for Cd, 12.09; and for Cr, 13.76, representing reductions in mobility of 83% for Ni, 76% for Pb, 50% for Cd, and 44% for Cr[6].

In the same experiments no effect of the organic amendments was detected with respect to the change in mobility of Hg. Previous[7] and current results indicate that both organophilicity and the hydrophilicity influence the movement of Hg in the environment.

The present investigation concern the mobility of heavy metals in soils and soil profiles in connection with soil humus content and quality. The effects of hydrophilicity and organophilicity on the movement of Hg in contaminated soils and sediments was also investigated.

MATERIALS AND METHODS

The new system[8] for the evaluation of the effects of humic substances on the retention of toxic elements and compounds used the new parameter "the environment protectional capacity of soils" (EPC_G), based on the concept that both humus content and humus quality influences the mobility of heavy metals in soils and in the environment. The EPC_G value included the humus quality parameter, the K-value (humus stability coefficient)[9].

The K-value is determined according to the following equation:

$$K = \frac{E_{NaF}}{E_{NaOH} \cdot H}$$

where E_{Naf} and E_{NaOH} are the extinction coefficients for humus extracts in 1% NaF and in 0.5% NaOH solutions. The E values are determined at 9 wavelengths in the visible spectra from 420 nm to 750 nm. H is the total humus content (%) of the soil determined by the dichromate method of Tyurin[10].

In the preparation of the NaOH and NaF extracts, air dried soils or river sediments (2 g soil or 2 g sediment) were mixed with 1% NaF solution or 0.5% NaOH solution (1:10 soil or sediment/solution). After 2–3 min shaking by hand, the samples were allowed the stand at room temperature for 48 h and filtered through MN 640 m filter paper. K-values were determined from the E_{NaF} and E_{NaOH} values.

EPC_G values for soil and sediment were calculated in the following way[11]:

$$EPC_G = D_X \cdot H^2 \cdot K$$

where D_X is the thickness of the investigated soil layer (cm).

The mobile concentration of a heavy metal was determined by the extraction method of Lakanen and Erviö with AcAA-EDTA and atomic absorption[12].

RESULTS AND CONCLUSIONS

The lowest K values were obtained for undegraded organic materials, e.g., forest litter. Characteristic values for such materials are in the range 0.01 to 0.001. Humus layers of

brown forest soils show values of 0.1 to 0.01, and Hungarian chernozem soils show the highest values, 1 to 10. Soils with high EPC_G values and deep humus layers with high K values show high capacity for the binding of toxic heavy metals and xenobiotics[13,14].

The results were evaluated in three contexts: with respect to the level of contamination due to industrial pollution in the investigated soil profiles; in relation to Pb contamination of soil near major traffic routes; and in relation to the distribution of mercury in the soil profiles as affected by ground water level and the accumulation of mercury in river sediments[15,16].

A new concept, the presumable risk in environmental contamination, was introduced through comparison of the EPC_G with the mobile amounts of contaminants in soil profiles and river sediments.

The main results can be summarized as follows:

Levels of contamination in soil profiles near industrial pollution sources

The heavy metal contaminations and their distribution in soil profiles are presented in Tables 1 and 2. Table 1 shows heavy metal contamination and their distribution in the soil profiles of the Central and North Transdanubion Industrial Districts. From the five selected soil profiles, two are in the neighbourhood of thermal electric generating plants, two are close to chemical industrial units, and one is remote from main traffic routes and industrial districts.

Pb contamination was strongly associated with the topsoil indicating notable organophilicity of this element.

Hg often appeared in the profiles near the water table or affected by ground water as is shown by the profile from Bokod in which Hg appears near the water table at 60–80 cm depth. Near the electric power plant in deeper layers of a sandy soil (poor in humus content), the Hg had moved down the profile (Tatabánya-Bánhida). The soil near Almásfüzitö, which was on alluvial chernozem on Danube sediments, also contained Hg in the deeper layers. Further from the riverbank of the Danube, near Nyergesujfalu, the effect of Hg accumulation in the profiles was very similar but more difficult to see because concentrations were low. Several hundred meters from the Danube, almost no Hg contamination was observed in the soil profile (Komárom-Acs).

The distribution of heavy metal contamination in soil layers was compared with their EPC_Gs (Figures 2 and 3) in the same layers.

EPC_G values for the investigated soil layers are shown in Figures 2 and 3. The values of Pb, Ni, and Cd contamination in the top layers are expressed in parallel in three groups of columns. Columns for Sajolád show, with the interruption of Pb and Cd columns, one range higher contamination than the other values in Figure 3. These values for Pb and Cd (Table 2) are Pb, 103.00–64.33, and for Cd, 6.16–4.89 mg/kg in the top layers.

The movement of Hg at low concentrations in the soil profiles is shown in Table 2. In the profile from Ozd-Bánréve, a slight increase in Hg values appears at 40–60 cm, as is shown in the Sajóbábony profile taken near from the chemical industrial unit.

The organophilicity of Ni is shown in Tables 1 and 2. Ni is not accumulated in the top layers because the plants do not need Ni or need it at very low levels, and accumulation of Ni in plant materials and plant residues does not occur. At higher amounts of Ni in the soil, the plants are killed before accumulation can appear. The organophilicity of Ni is thus expected to be different from that for Pb.

The distribution of Cd is different. Cd is the most mobile among the three mentioned elements (Pb, Ni, Cd) and showed slight organophilicity. Cd contamination occurs

Table 1 The distribution of mobile amounts of toxic heavy metals in soil profiles in the Central and North-Transdanubian Industrial District of Hungary.

Soil profiles	*No*	*Investigated layer in cm*	*Pb*	*Ni*	*Cd*	*Hg*
			in mg/kg soil			
Bokod[a]	26	0–10	9,33	4,84	0,12	0,00
		10–20	9,07	5,10	0,07	0,00
		20–40	5,61	5,23	0,06	0,00
		40–60	4,26	3,73	0,15	0,49
		60–80	3,20	2,32	0,13	0,56
		80–100	3,29	1,17	0,11	0,53
		100–120	3.44	0.47	0.12	0.65
Tatabánya-Bánhida[b]	27	0–10	3,65	0,68	0,09	0,25
		10–20	4,31	0,93	0,11	0,18
		20–40	4,30	0,62	0,17	0,31
		40–60	1,44	1,11	0,01	0,12
		60–80	1,09	1,17	0,01	0,19
		80–100	1,40	1,05	0,03	0,26
Almásfüzitö[c]	1	0–10	3,68	1,53	0,08	0,27
		10–20	3,68	1,53	0,09	0,32
		20–40	3,50	1,53	0,05	0,35
		40–60	2,27	1,27	0,04	0,34
		60–80	0,88	1,02	0,02	0,46
Nyergesujfalu[d]	39	0–10	6,36	3,16	0,10	0,02
		10–20	3,96	3,98	0,08	0,06
		20–40	1,81	3,71	0,05	0,01
		40–60	0,90	2,28	0,03	0,01
		60–80	1,39	0,95	0,09	0,09
		80–100	2,17	0,30	0,11	0,06
Komárom-Ács[e]	41	0–10	4,15	1,36	0,11	0,01
		10–20	3,84	1,36	0,11	0,01
		20–40	3,81	1,41	0,11	0,01
		40–60	3,39	0,94	0,11	0,01

[a]near the Bánhida electric power plant, beside the cooling pond; groundwater level 80 cm.
[b]deep lying area on the edge of the town; beside the electric power plant.
[c]400 m from the Central Industrial Unit (chemical industry); 300 m from river bank.
[d]500 m east of Danube on alluvial chernozem; east of Plastic Industrial Center
[e]800 m from Danube on alluvial chernozem between the road and the river.

mostly as air pollution from electrical power plants or chemical industrial units. Much less but sometimes considerable amounts are distributed near roads.

High contamination of soil profiles and river sediments in the North-East Industrial District of Hungary by the river Sajó was detected. Cd was concentrated above the toxic level in the soil profile at Sajópetri (meadow soil on river sediments) and in the river sediments of Sajó, near Sajólád (Table 2).

The river sediments at Sajó showed the highest Hg contamination. The contamination down the river Sajó in the soils and sediments was also investigated. A decrease was observed with increasing distance along the river. That was also evident from the soil contaminations near Muhi on meadow chernozems developed on the overflowed area at Sajó. Several km to the South on the riverbank, the accumulation of Hg and Cd was much decreased (see the profile from Nagycsécs).

Table 2 The distribution of mobile amounts of toxic heavy metals in soil profiles in the North-East Industrial District of Hungary.

Soil profiles	*No*	*Investigated layer in cm*	*Pb*	*Ni*	*Cd*	*Hg*
			in mg/kg soil			
Ózd-Bánréve	76	0–10	5,80	2,08	0,07	0,05
on the border of Ózd		10–20	4,92	2,76	0,09	0,02
in green belt		20–40	2,24	2,35	0,07	0,08
near smaller		40–60	1,87	2,24	0,02	0,09
industrial units		60–80	2,24	3,72	0,04	0,06
		80–100	2,58	3,18	0,04	0,06
Sajóbábony	87	0–10	4,83	2,20	0,19	0,01
200 m from Chemical		10–20	3,32	1,87	0,16	0,02
Industrial Unit on		20–40	2,21	1,32	0,09	0,07
a meadow beside a hill		40–60	2,02	1,32	0,04	0,07
		60–80	2,19	1,25	0,01	0,01
		80–100	2,12	1,76	0,01	0,01
Rudabánya	88	0–10	80,83	1,28	0,19	0,28
Pretreatment unit of		10–20	42,04	1,95	0,17	0,17
ores (200 m from		20–40	39,71	2,69	0,15	0,12
the Factory)		40–60	6,72	1,10	0,02	0,05
		60–80	3,99	0,90	0,07	0,02
Diósgyör	89	0–10	51,24	2,55	0,51	0,17
beside the electrical		10–20	35,00	2,88	0,19	0,17
power plant		20–40	26,81	2,89	0,01	0,14
Sajópetri	90	0–10	83,91	2,31	4,34	0,66
Sajó river sediment						
Sajólád	91	0–10	103,00	2,57	6,16	0,40
riverbank, soil on		10–20	75,70	2,84	6,45	0,88
river sediments,		20–40	48,91	1,44	7,48	0,86
meadow		40–50	64,33	1,24	4,89	0,98
Muhi	92	0–10	5,95	4,40	0,31	0,10
meadow soil on river		10–20	3,42	5,00	0,18	0,06
sediments 400 m from		20–40	2,29	5,87	0,11	0,05
River Sajó, 20 km		40–60	1,70	5,38	0,09	0,02
from Sajólád		60–80	1,83	5,45	0,06	0,03
		80–100	1,61	5,52	0,04	0,01
Nagycsécs	93	0–10	1,97	0,73	0,04	0,01
river branch of Sajó		10–20	3,55	1,12	0,05	0,04
immediatly in riverbank		20–40	2,83	0,53	0,03	0,02
sediment		40–60	1,96	0,59	0,05	0,01

Pb contamination near major traffic routes

The organophilicity in distribution of Pb is shown by its distribution in Figure 1. On Highway M-7, Pb is strongly associated with the surface layers and its mobility in the profiles is very low.

In Figure 1b, the movement of Pb in the air from the road was influenced by the shape of the soil surface and by the flow patterns of the air.

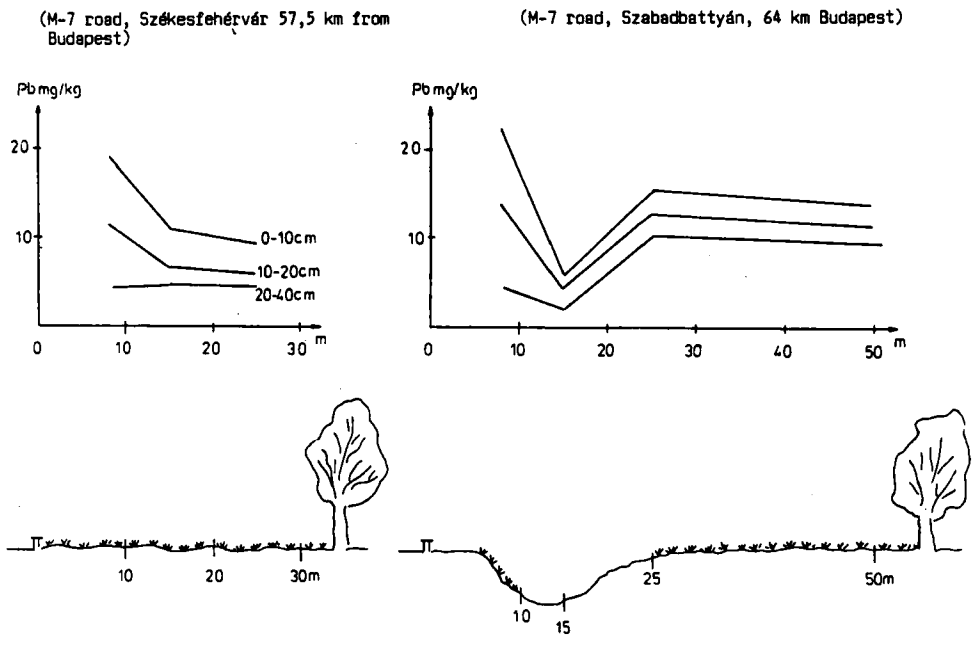


Figure 1 Pb contamination depending on distance from the investigated roads and in depth in soil profiles

A clear rule linking EPC_Gs of soils with toxic metal distribution can be seen in Figure 2. The differences in the organophilicity of Pb, Ni and Cd was associated with big differences in the distribution of these heavy metals in soil profiles; Pb was the most organophilic and was associated with layers with high EPC_Gs. The mobile amount of Pb decreased in the layers with high EPC_G values and increased for low EPC_Gs. Where the EPC_G values were low, the mobility of the metal was relatively greater. Ni and Cd showed similar but very slight organophilicity.

Mercury in soil profiles and river sediments

The most important conclusions of our results are summarized in Figures 3a, 3b, and 3c in which the EPC_G values of the soil profile layers are compared with the levels of mobile heavy metals. The comparison of these values in the profiles and soil layers leads to a general rule. The differences in the risk of environmental contamination depends on the EPC_Gs of the soils.

Figure 3a corresponds to the highest risk of contamination. The lowest EPC_Gs of soils were associated with high mobility of heavy metal contaminants in the soil profile. Intermediate EPC_G values are associated with middle levels of contamination (Figure 3b) and moderate risk. Figure 3c shows the lowest risk of environmental contamination. High EPC_G values are associated with low contamination levels and low risk.

Further investigations will extend these results to enable better evaluation of the risk of environmental contamination in soils and sediments.

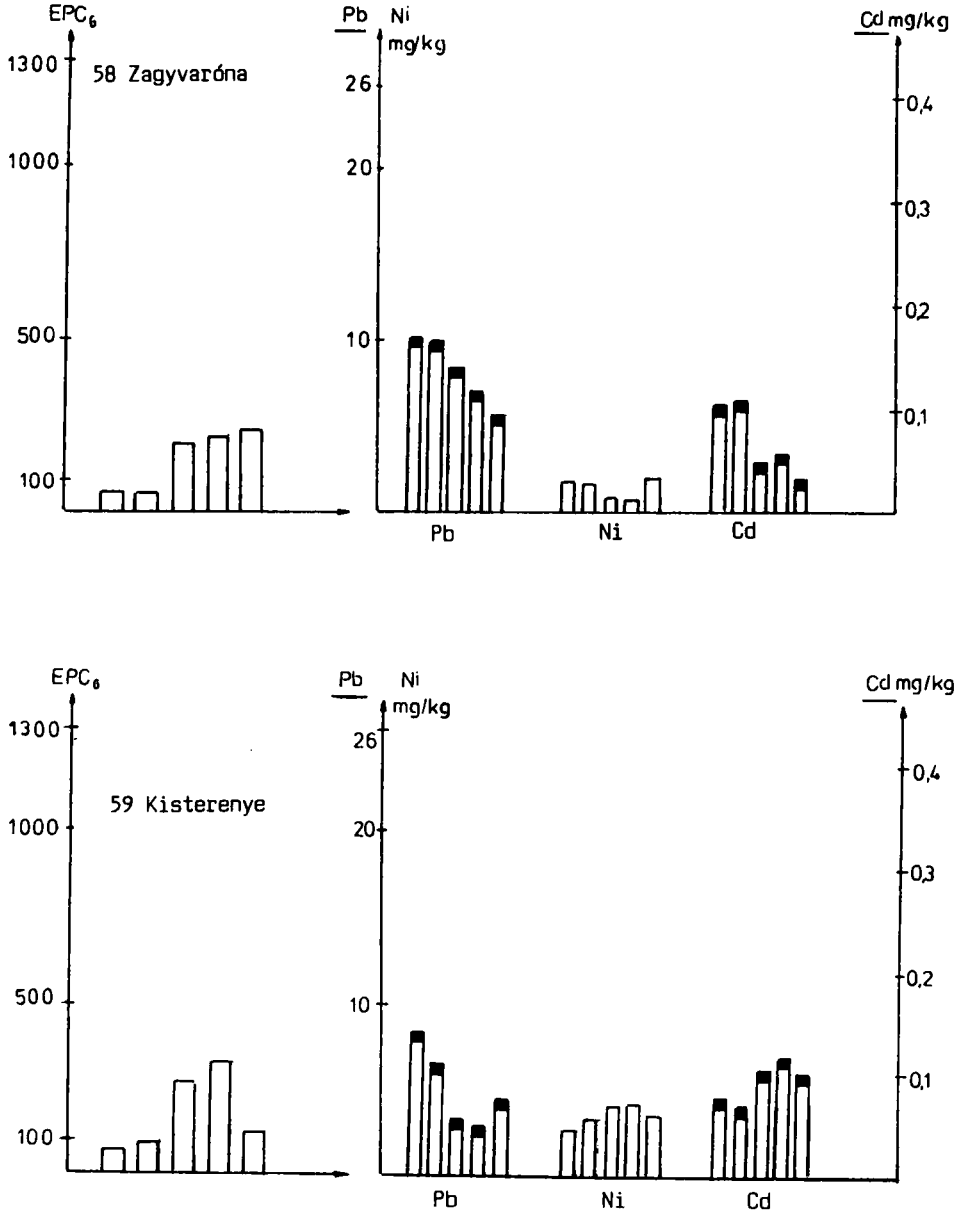
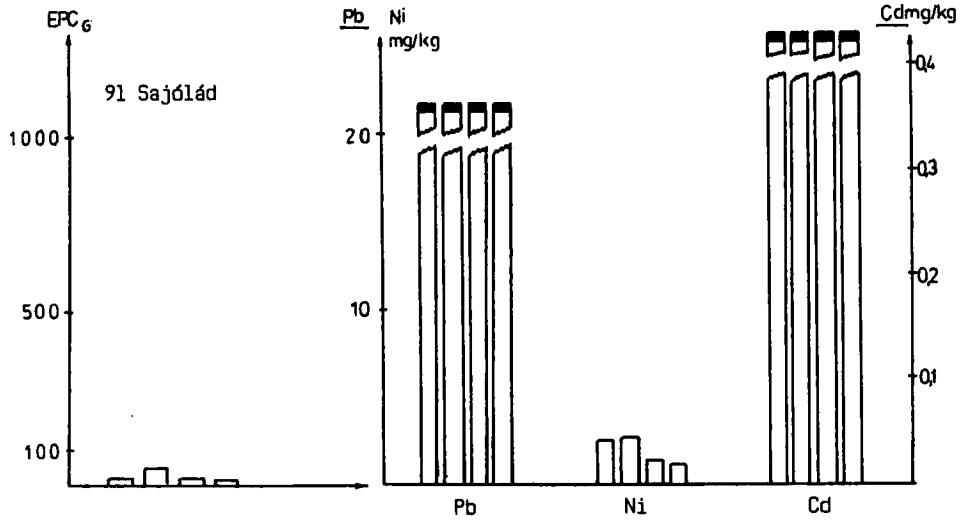
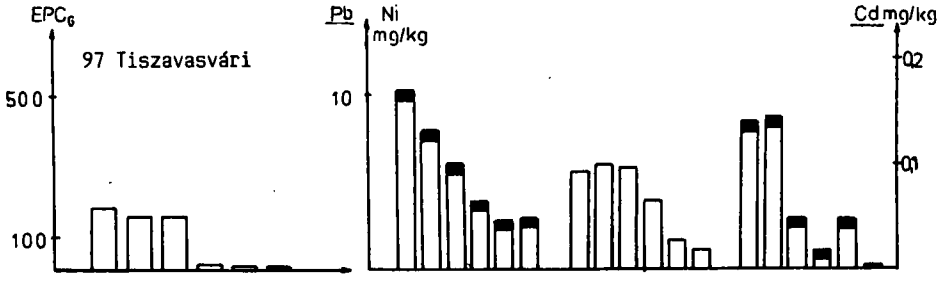


Figure 2 Relationships between environment protectional capacity of soils and organophility of heavy metal contaminations (their distribution in soil profiles expressed in mobile amounts).

A. High risk: low EPC_G values with high level of contamination



B. Moderate risk: Middle values of EPC_G with middle level of contamination



C. Low risk: High EPC_G values with low level of contamination

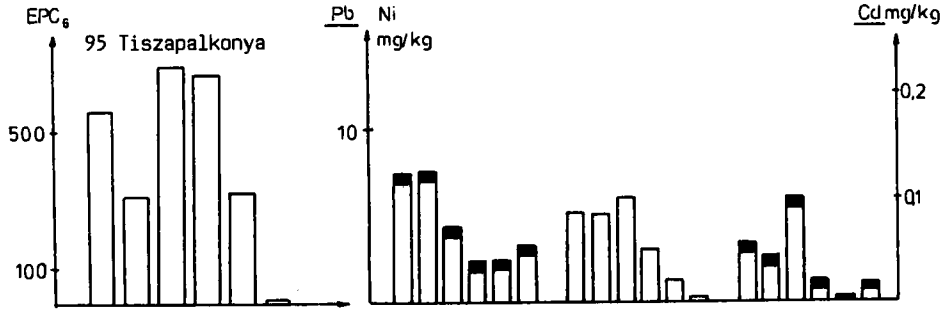


Figure 3 The risk of environmental contamination: EPC_G values of soils compared to their contamination with heavy metals (expressed in mobile amounts).

References

1. A. Ng and C. Patterson, *Geochim. Cosmochim. Acta,* **45**, 2109–2121 (1981).
2. U. Förstner, in *Changing Metal Cycles and Human Health* (J. O. Nriagu, Dahlem Konferenzrn, Eds., Springer Verlag, Heidelberg, 1984) pp. 71–94,
3. F. M. Nikiforova and R. S. Smirnova, *Acta of International Conference on Heavy Metals in the Environment,* Toronto Vol. C. pp. 94–96 (1975).
4. U. Förstner, in *The Importance of Chemical Speciation in Environmental Processes,* (M. Bernhard, F. E. Brinckman, and P. J. Sadler, eds., Springer Verlag, Heidelberg) pp. 465–491 (1986).
5. L. Hargitai, *Sci. Total Environ.,* **81/82**, 643/651 (1989).
6. L. Hargitai, *Proceedings of International Symposium on Humus et Planta* (CSVTS ed., Prague, 1988) p. 78.
7. L. Hargitai, *Transactions of the 14th International Congress of Soil Science,* Kyoto, Vol. II. Comm. II 102–107 (1990).
8. L. Hargitai, *Publ. Univ. Horticult. Budapest,* **45**, 113–118 (1981).
9. L. Hargitai, összehasonlitó szervesanyag-vizsgálatok különbözo talajtipusokon optikai módszerekkel (Vergleichende Humusuntersuchungen in verschiedenen Bodentypen mit optischen Methoden) *Agártud. Egy. Agron. Kar Kiadv.* **2**, #10, 1–27 (1955).
10. I. V. Tyurin, *Organicseszkoje Vescsesztvo Pocvsy,* Seljhozgiz, Moscow (1937).
11. L. Hargitai, *Publ. Univ. Horticult. Budapest,* **47**, 139–145 (1983).
12. L. Hargitai *et al.,* in *Humic Substances and their Role in The Environment* (H. Frimmel-R. Christman, Dahlem Konferenzen, ed., John Wiley New York, 1987) pp. 245–256.
13. E. Lakanen and R. Ervio, *Acta Agr. Fennica* **123**, 223–232 (1971).
14. L. Hargitai, *Transactions of the 12th Int. Congr. of Soil Science (Abstracts of Papers)* New-Delhi, 1982, p. 31.
15. T. Asami, in *Changing Metal Cycles and Human Health* (J. O. Nriagu, Dahlem Konferenzen, ed. Springer Verlag, Heidelberg, 1984) pp. 95–111.
16. A. Kloke-P. L. Sauerbeck and H. Vetter, in *Changing Metal Cycles and Human Health* (J. O. Nriagu, Dahlem Konferenzen, ed. Springer Verlag, Heidelberg, 1984) pp. 113–141.