

DISTRIBUTION OF CU, NI, PB, AND ZN IN NATURAL BROWN FOREST SOIL PROFILES FROM THE CSERHÁT MTS., NE HUNGARY

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ABSTRACT

Distributions of total and bioavailable amounts of heavy metals (Cu, Ni, Pb, Zn) were studied in four brown forest soil profiles developed on different types of bedrock. In the study area (Cserhát Mts., NE Hungary) facilities are provided to recognize the role of bedrock and pedogenic processes in the distribution of heavy metals in soils characterized by natural background level of heavy metals.

Distribution of total and soluble metal concentrations are generally similar in the studied profiles, differences were observed only in case of zinc. Among the studied metals the following bioavailability sequence was observed: Pb (25% of total Pb) > Cu (20% of total Cu) > Ni (10% of total Ni) > Zn (2.5% of total Zn).

The obvious effect of organic matter on trace metal distribution is supported by its influence on the distributions of Pb and Zn. Distributions of Cu and Zn is determined by the presence of amorphous Al and Fe oxides. The stronger retention of trace metals by clay minerals is suggested by the good negative correlation of clay mineral and available Pb, Ni, and Zn contents of soils. Clay minerals and organic matter have contrary effect on heavy metal retention in soils.

There are factors dependent (e.g. clay minerals) on and independent (e.g. organic matter) of bedrock, of which common effect forms the actual distribution of heavy metals in soils.

Key words: soil geochemistry, heavy metal distribution, bedrock effect, brown forest soils.

INTRODUCTION

Soils formed under different pedogeneses show considerably different trace element distribution in their profiles. However, different soil types showing similar trace element distribution may differ in vertical metal distribution as a result of differences in metal extractability (Fujikawa et al., 2000). Parent material composition largely influences the contents of heavy metals in most of soils (Pasiieczna and Lis, 1999; Davies et al., 1999), except e.g. by that carbonate free soil types, which are markedly enriched in heavy metals with respect to the underlying calcareous rock types. Heavy metal enrichment in these soils is associated with the formation of Fe-Mn oxides and clay accumulation (Palumbo et al., 2000). Besides amorphous oxides and clay minerals, organic matter is of important role in heavy metal retention in surface soil horizons (Tack et al., 1997). In addition, the anthropogenic contamination also enhances the amount of heavy metals in the topsoil (Baize and Streckeman, 2001).

De Matos et al. (2001) found that soil types and soil horizons influence the metal retardation in soils which, in turn, correlates better with the chemical than the mineralogical characteristics of soils. These chemical characteristics are greatly influenced by soil pH, which has important effect on behavior of metals in soils (Maskall and Thornton, 1996). The alkalisng effect of carbonates may also influence the mobility and retention of some heavy metals through precipitation (Echeverría et al., 1998). Gomes et al. (2001) observed that soil characteristics that may have affected the adsorption of heavy metals were organic carbon, clay and gibbsite contents for Cu, pH and cation exchange capacity for Ni and Pb, as well as iron oxides for Zn.

In this paper we study the distribution of Cu, Ni, Pb, and Zn in natural forest soils from the Cserhát Mountains, NE Hungary. The study area is characterized by various geological formations (Neogene volcanics and molasses sediments) which are covered by forest soil types, such as brown forest soils (60%), brown earths (30%), as well as stony soils (10%). They have mostly loam texture and low hydraulic conductivity (Marosi and Somogyi, 1990). These soils are often characterized by the same pedogenic process, such as clay illuviation (Stefanovits, 1971). The study area is almost free of anthropogenic contamination, it is far from the main roads and industrial activities. These facts provide facilities to recognize the role of soil parent material and the pedogenic processes in the distribution of heavy metals in soils characterized by the natural background level of heavy metals.

MATERIALS AND METHODS

Four forest soil profiles developed on siltstone (P09), sandstone (P14), limestone (P15), and andesite (P16) were studied with respect to heavy metal distribution (Fig. 1). Samples were collected by hand drill for laboratory analyses. Air dried samples were passed through a 2 mm sieve. The clay fractions of samples were separated by sedimentation from aqueous suspensions.

Soil particle size was determined by a simplified pipette method after Kettler et al. (2001). Soil pH was measured potentiometrically in 1:2.5 suspension (soil:distilled water). The analysis of organic carbon was performed using the Rock-Eval method. Mineralogical composition of samples was identified by powder X-ray diffraction (Philips PW1710). Major elements were determined by X-ray

fluorescence spectrometry (Philips PW1410), while total and bioavailable heavy metal concentrations were measured by atomic absorption spectrometry (Perkin-Elmer AAnalyst 300). Total element concentrations were dissolved using the mixture of nitric-acid and hydrogen-peroxide with microwave digestion system, while bioavailable amounts of heavy metals were digested using the Lakanen-Erviö method (mixture of EDTA, acetic-acid and ammonium-hydroxide) according to the Hungarian standard methods (MSZ 21470-50: 1998).

RESULTS AND DISCUSSION

Soil composition

Characteristics of the studied soil profiles are summarised in Table 1. Soil P14 is a Cambisol with loam texture, while the other ones are Luvisols having silt loam texture (Driessen et al., 2001). Soil on siltstone is characterized by the highest organic matter content (up to 6.74%), the other profiles contain maximum half of this amount. The organic matter content in the B horizons exceeds 1% only in one case (soil P15).

The mineralogical compositions of the studied profiles are dominated by inherited minerals, such as quartz (50-80%) and feldspars (up to 20%). In some cases (P14 and P16) pyroxene and amphibole appear in traces. Significant amounts of calcite were found in the subsoil of profiles on siltstone and on limestone (up to 30% and 50%, respectively).

Although most of the studied profiles (P09, P15, P16) are characterized by an argic horizon (Driessen et al., 2001), their clay mineralogical compositions are largely different. These profiles contain similar quantities of clay minerals (up to 25%), which have a maximum in B horizon (P09 and P15), or their amounts increase with depth (P14 and P16).

In soil on siltstone there are vermiculite and chlorite/vermiculite intergrade mineral species with increasing chlorite component downward, and a small amount of illite. In soil on sandstone besides the dominating low charge montmorillonite, discrete illite and illite/smectite mixed layer species appear in the topsoil. In the upper part of soil on limestone the "poorly crystallized" low charge montmorillonite dominates, while below 70 cm high charge montmorillonite enters in its place. In the top of soil on andesite vermiculite and illite are the dominating species, while below 40 cm the low charge montmorillonite dominates.

Soil chemistry

Three of the studied profiles (P09, P14, and P15) are characterized by acidic topsoil and alkaline subsoil, and an abrupt change in soil pH below the B horizons. Soil on andesite has an acidic pH increasing with depth within a narrow range (Table 1).

Total and bioavailable heavy metal concentrations of soils are shown in Table 2. The lowest values of heavy metals are found in soil on sandstone and on limestone. However, in case of soil on limestone the amount of lead is the highest. The highest values are generally measured in soil on andesite. Soil on siltstone contains higher amount of Ni and Zn, and lower amount of Pb and Cu as compared to the other profiles. All of four elements were within the range reported as typical average concentrations in soils (Adriano, 1986).

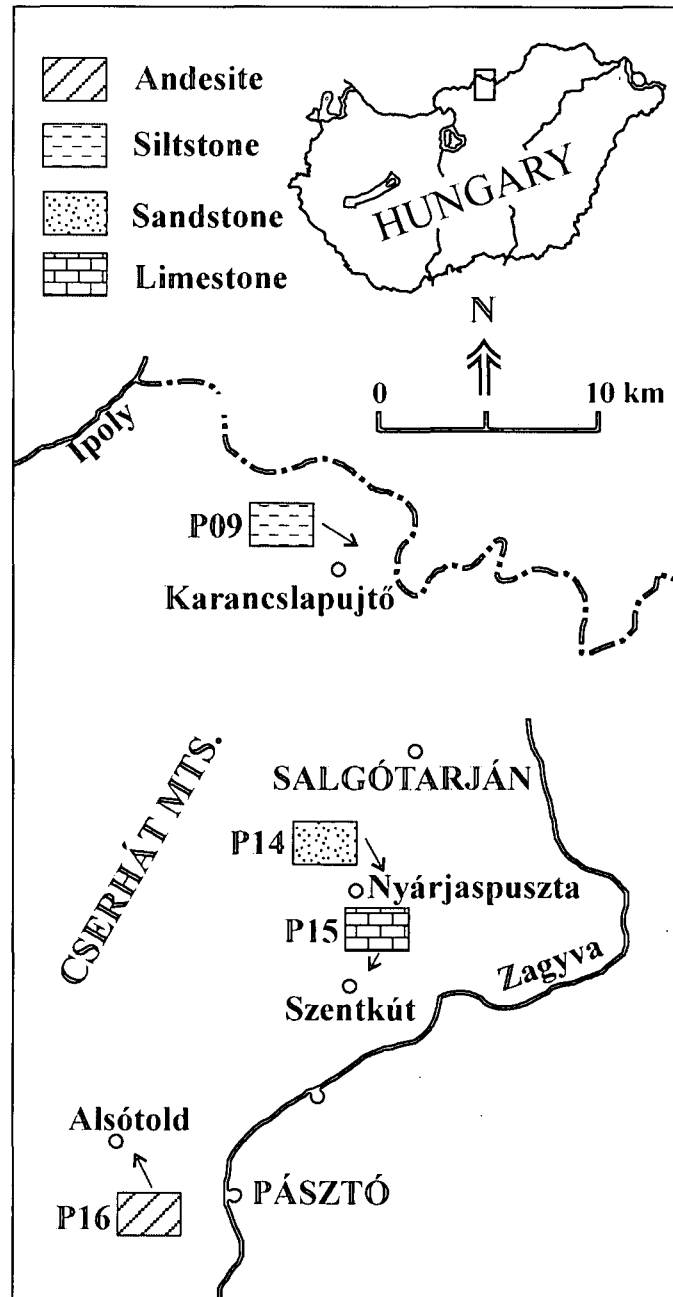


Fig. 1. Sketch map showing the study area and the sampling sites.

The most easily extractable metal is lead, its 25% is available for plants, while only 2.5% of total zinc is soluble. The copper and nickel are characterized medium bioavailability, 20% and 10% of their total amount is available for plants, respectively. Soil on siltstone is characterized by the lowest extractability, except in case of Pb, which is at least available metal in soil on andesite. According to Fujikawa and Fukui (2001) the binding of Cu, Ni, Pb and Zn to soil organic matter in forest soils is higher than in other soil types causing higher availability. The bioavailabilities of heavy metals are shown in Table 3 and Table 4.

Characterization of Al, Fe, and Mn distribution is also necessary, because of their significant effect on trace metal retention in soils. The distribution of Al and Fe is very similar in all of the studied profiles, these two elements correlate well with each other ($r = 0.90$). They have a

Table 1. Some physico-chemical properties of the studied soil profiles.

P	H	Depth cm	Sample No.	Depth cm	Colour	pH _{H2O}	Texture (%)			TOC %	Carb %	Relative amounts of CM in clay fractions (%)				
							Sand	Silt	Clay			Montm	Verm	Ill	Chl	Kao
P09	A	0-10	911	5	10YR 3/4	5.66	41	51	8	6.74	15	65	35			
			912	15	7.5YR 5/8	6.39	28	60	12	0.92		75	25			
	913	35	10YR 5/8	6.85	26	63	11	0.39	80	20						
	BC	40-60	914	50	10YR 6/8	8.08	37	54	9	<0.10		20	80			
			915	70	2.5YR 6/4	8.41	43	50	7	<0.10		30	25	75		
P14	A	0-40	1411	5	10YR 4/2	5.33	40	49	11	2.90	50	35	15			
			1412	30	10YR 4/4	5.88	41	48	11	0.62	70	20	10			
			1413	60	10YR 5/6	5.59	41	48	11	0.25	80	15	5			
			1414	80	5.59	75	20	5								
	B	40-200	1415	100	10YR 5/6	5.67	46	45	9	0.11	75	20	5			
			1416	140	6.30	75	20	5								
			1417	180	10YR 5/6	6.81	57	36	6	<0.10	70	25	5			
	C	200-240	1418	210	8.68	80	15	5								
			1419	230	2.5YR 6/4	8.77	50	44	6	<0.10	65	30	5			
	P15	A	0-20	1511	5	10YR 3/3	5.27	29	61	11	3.48	55	35	10		
1512				15	10YR 6/3	5.60	2.59	55	30	15						
1513				40	10YR 4/4	5.27	9	76	14	1.06	70	20	10			
B		20-100	1514	60	5.39	70	20	10								
			1515	80	10YR 5/4	5.67	8	76	17	0.95	70	20	10			
			1516	100	6.17	60	30	10								
C		10-120	1517	110	10YR 6/4	7.84	32	60	9	0.80	70	20	10			
P16	A	0-40	1611	5	10YR 3/3	5.84	24	67	9	2.29	15	40	30	15		
			1612	15	10YR 3/2	6.07	1.80	10	40	30	20					
			1613	35	10YR 3/2	6.30	5	87	9	1.66	10	35	35	20		
			1614	50	6.30	15	35	35	15							
	B	40-130	1615	70	7.5YR 4/2	6.28	4	82	13	1.05	40	20	30	10		
			1616	90	6.10	60	10	15	15							
			1617	110	10YR 5/6	6.03	7	80	13	0.35	60	10	15			
			1618	120	5.91	65	5	20	10							
	C	130-150	1619	140	2.5YR 5/4	6.12	6	82	12	0.32	60	5	20	15		
			16110	150	6.42	0.25	65	0	20	15	5					

P = profile, H = horizon, TOC = total organic carbon, Carb = carbonate minerals, CM = clay minerals, Montm = montmorillonite, Verm = vermiculite, Ill = illite, Chl = chlorite, Kao = kaolinite.

Table 2. Concentrations of Al, Fe, Mn, and Cu, Ni, Pb, Zn, as well as the available amounts of trace metals in the studied profiles.

Profile	Sample No.	Depth cm	Al ₂ O ₃	Fe ₂ O ₃	Mn	Cu	Cu _A	Ni	Ni _A	Pb	Pb _A	Zn	Zn _A
			Wt. %		ppm								
P09	911	5	12.33	4.66	469	13	1.7	28	2.1	27	15.1	87	8.0
	912	15	16.45	6.39	330	15	1.1	36	1.0	21	3.5	92	<1.0
	913	35	16.30	6.76	444	16	2.6	42	1.5	15	<1.0	94	<1.0
	914	50	13.72	5.03	333	8	1.1	35	3.2	5	<1.0	76	1.7
	915	70	10.09	3.40	203	7	<1.0	26	1.1	3	<1.0	59	<1.0
P14	1411	5	9.82	2.90	602	6	1.9	22	2.9	22	10.1	42	3.5
	1412	30	12.28	4.02	248	5	<1.0	25	1.2	18	4.5	47	<1.0
	1413	60	12.24	4.69	184	6		27		20		54	
	1414	80	10.88	4.11	249	4	<1.0	24	<1.0	18	3.2	43	<1.0
	1415	100	10.97	3.79	289	4		25		19		42	
	1416	140	11.16	3.88	437	4	<1.0	28	1.8	12	3.0	47	<1.0
	1417	180	9.84	3.33	389	3	<1.0	31	3.5	8	2.9	42	<1.0
	1418	210	10.47	3.43	501	2	<1.0	27	5.8	12	3.8	40	<1.0
	1419	230	10.64	3.55	498	4		27		15		47	
P15	1511	5	13.15	4.84	1142	12	3.3	21	2.9	37	14.1	71	3.3
	1512	15	13.94	5.11	1043	13	3.0	23	2.3	30	9.3	69	2.4
	1513	40	14.72	5.77	451	13	4.8	24	2.3	24	5.9	70	1.5
	1514	60	14.79	5.75	525	14		25		21		69	
	1515	80	15.47	6.03	624	14	2.3	27	1.6	20	4.9	67	<1.0
	1516	100	15.34	6.14	434	16		30		21		66	
	1517	110	10.40	3.09	277	11	1.2	26	1.2	19	5.4	49	<1.0
P16	1611	5	13.10	6.49	1683	25	5.6	24	4.6	32	4.4	67	5.3
	1612	15	13.11	5.99	1781	23		24		32		66	
	1613	35	12.05	5.10	2021	19	5.0	26	7.6	27	7.3	62	3.3
	1614	50	13.98	5.86	1414	20		26		23		68	
	1615	70	15.13	6.85	868	22		26		20		72	
	1616	90	15.83	7.44	386	25	3.0	24	<1.0	19	<1.0	72	<1.0
	1617	110	15.48	7.28	428	25		24		21		71	
	1618	120	15.13	7.04	405	26		22		20		69	
	1619	140	15.05	7.38	997	29	7.9	28	<1.0	21	<1.0	72	0.0
	16110	150	16.47	9.90	1323	60		61		23		80	
Range			9.82-16.47	2.90-9.90	184-2021	2-60	0.4-7.9	21-61	0.6-7.6	3-37	0.8-15.1	40-94	0-8.0
Average			13.24	5.36	677	15	2.4	28	2.4	20	5.1	63	1.6
Median			13.15	5.11	451	13	1.8	26	2.0	20	4.1	67	0.7

Table 3. Relative extractability (in brackets in %) of Cu, Ni, Pb, and Zn in the studied soils by the Lakanen-Erviö digestion. R. E. = relative extractability.

Profile	P09			P14			P15			P16		
	A	B	C	A	B	C	A	B	C	A	B	C
Very High (>50%)	Pb (56)											
High (25-50%)			Pb (27)	Pb (36)		Pb (43)	Pb (35) Cu (26)	Pb (25)	Pb (28)			Cu (27)
Medium (10-25%)	Cu (13)	Pb (17) Cu (12)	Cu (13)	Cu (124)	Pb (22) Cu (15)	Cu (19) Ni (16)	Ni (12)	Cu (16)	Cu (11)	Cu (24) Ni (24) Pb (21)	Cu (12)	
Low (1-10%)	Ni (7.5) Zn (9.2)	Ni (3.2)	Ni (4.2) Zn (1.6)	Ni (8.9) Zn (4.5)	Ni (4.7)		Zn (4.1)	Ni (5.9)	Ni (4.6)	Zn (6.6)	Pb (4.2) Ni (2.5)	Pb (3.8) Ni (2.5)
Very low (<1%)		Zn (0.43)			Zn (0.22)	Zn (0.29)		Zn (0.15)	Zn (0.20)		Zn (0.92)	Zn (0.04)

maximum in the top of B horizon (P09 and P14), or their amount decreases with depth, and there is a significant change at the boundary of soil and its parent material. The amounts of these two elements depleted in soil on andesite, contrarily, they increased in soil on limestone, as compared to the parent materials. In the latter two profiles, Mn is distributed similarly to the previous elements, while in the other profiles uniformly.

Distribution of heavy metals in soil profiles

Copper

Copper is retained in soils through ion exchange and specific adsorption mechanisms. Cavallaro and McBride (1978) suggested that a clay mineral exchange phase may serve as a sink for Cu in noncalcareous soils. In calcareous soils, specific adsorption of Cu on CaCO₃ surfaces may control Cu concentration in solution. Copper also has a high affinity for soluble organic ligands and the formation of these complexes may greatly increase Cu mobility in soils (Dudley et al., 1991).

Distributions of the studied elements are shown in Fig. 2. Correlation between the different total and extractable metal concentrations and some physico-chemical properties of studied soils are presented in Table 4. In general, the distribution of copper in the studied profiles is uniform, except in soil on siltstone where this element shows a slight maximum in the B horizon. In case of profiles developed on carbonate containing rocks Cu significantly concentrates in the soil as compared to the parent material, while in case of soil formed on andesite there is a strong depletion of Cu in the soil.

Copper usually correlates well with Al and Fe in the studied profiles, except in case of soil on sandstone, where no relation was found among the different element distributions. In some cases (P09 and P16) its distribution is very similar to zinc and nickel. In general, the amount of copper slightly increases with the increasing clay mineral content of the studied samples. In soil on siltstone the copper content decreases as its carbonate content increases.

Table 4. Average relative extractability of Cu, Ni, Pb and Zn in the studied profiles by the Lakanen-Erviö digestion

	P09	P14	P15	P16
Cu	12	21	20	22
Ni	4.5	9.6	8.6	13
Pb	26	32	31	12
Zn	2.9	2.4	2.1	3.5

The amount of bioavailable Cu ranges between 7 and 37% of total copper content in the studied soils. The distribution of total and soluble copper contents is similar to each other within the profiles. The composition of soils has no effect on the available copper contents of soils.

Lead

Soluble lead added to the soil reacts with clays, phosphates, sulphates, carbonates, hydroxides, and organic matter, such that Pb solubility is greatly reduced due to adsorption as well as precipitation (McLean and Bledsoe, 1992). At pH values above 6, lead is either adsorbed on clay surfaces or forms lead carbonate. Puls et al. (1991) have demonstrated decrease sorption of Pb in the presence of complexing ligands and competing cations. Lead has a strong affinity for organic ligands and the formation of such complexes may greatly increase the mobility of Pb in soil.

The amount of lead in the studied profiles always decreases with depth independent of mineralogical composition of soils. Its amount correlates well with the total organic matter content of soil in all profiles: least of all in soil on sandstone, and most of all in soil on limestone. The lead does not correlate with one of the studied elements in these soil profiles, and it does not show correlation with the amount of clay minerals in the studied profiles either. In soil on siltstone the amount of lead increases as its calcite content decreases.

Among the studied metals lead is the most easily available metal for plants: up to 56% of total lead content of soils is extractable by the Lakanen-Erviö digest. The high amount of soluble lead in the upper part of profile P09 is due to the fact that there is a significant amount of lead bound to organic matter. This soil horizon is characterized by the highest organic matter content, which can accumulate lead from different sources (natural and atmospheric fallout). The amount of soluble lead decreases with depth within the soil profiles, and increases with organic matter content of soils, because the lead bound to organic matter can be easily desorbed by chelating agents (like EDTA in the Lakanen-Erviö solution). However, in most of studied profiles (P14, P15, P16) its amount decreases with increasing clay mineral content, suggesting the stronger binding of lead to clay minerals as compared to soil organic matter, showing that these two compounds have contrary effect on the available amount of lead in soils.

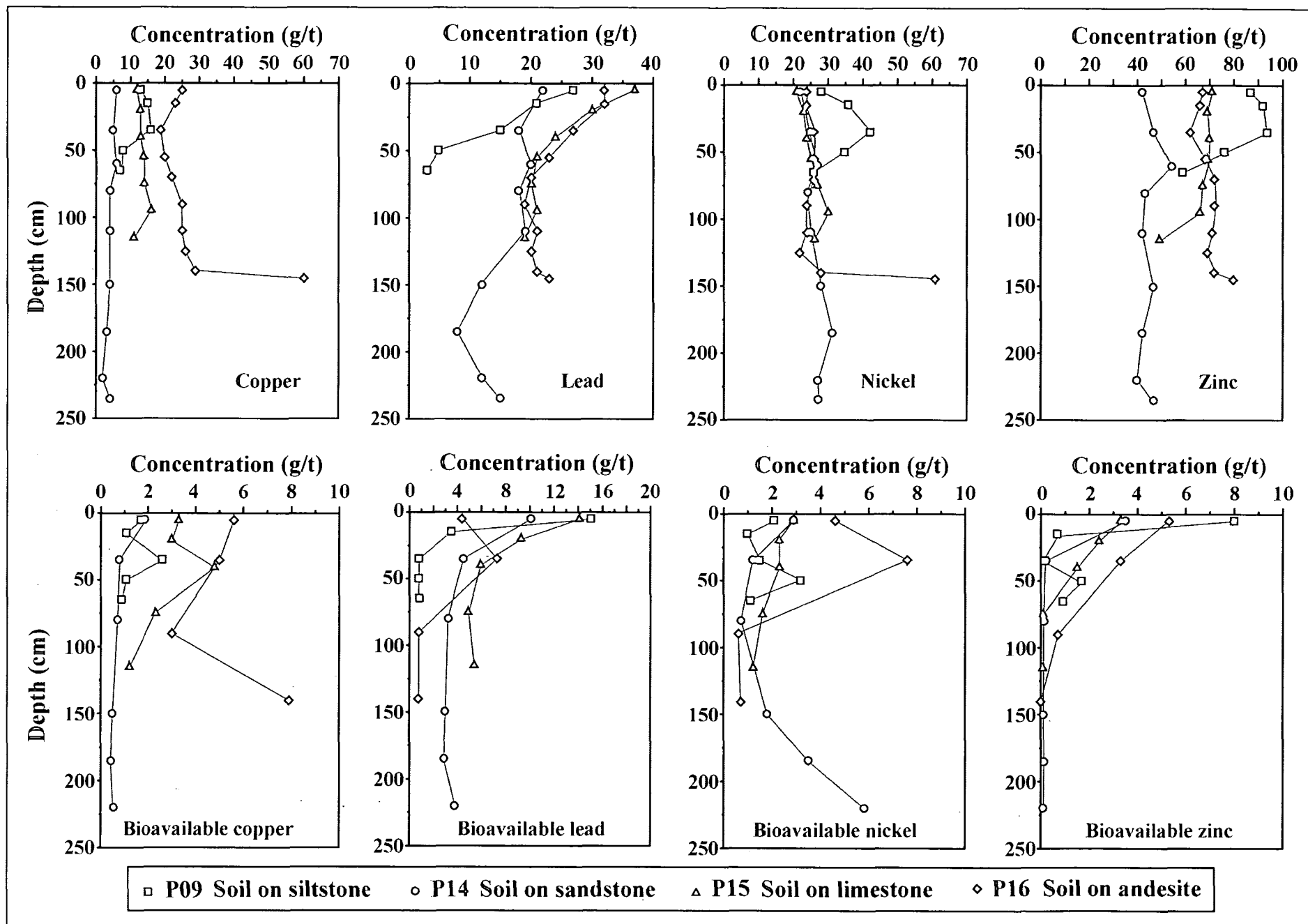


Fig. 2. Distribution of total and available amounts of Cu, Ni, Pb, and Zn in the studied profiles.

Nickel

Nickel does not form insoluble precipitates in unpolluted soils, therefore, the retention of Ni is proceeded exclusively through adsorption mechanisms. Nickel will adsorb to clays, iron and manganese oxides, and organic matter and it is thus removed from the soil solution. The formation of complexes of Ni with both inorganic and organic ligands will increase Ni mobility in soils (McLean and Bledsoe, 1992).

The distribution of nickel is very similar to that of copper, but in soil on siltstone Ni enriches significantly in the B horizon. The amount of Ni is near twofold in this horizon as compared to the other ones. In profiles formed on carbonate containing rocks nickel significantly enriches in the soil, while in case of soil on andesite there is a strong depletion of Ni as compared to the parent material.

In two profiles (P14 and P15) significant negative correlation between the nickel concentration and organic matter content of soils was found. The amount of nickel follows the distribution of Al and Fe, but less close as the amount of copper or zinc does. The amount of nickel shows slight increase with increasing clay mineral content, and their correlation are better in cases of soil developed on siltstone and on limestone.

The amount of soluble nickel (3-29% of total lead) does not correlate with the total nickel contents of soils, its distribution is usually uniform. There are no general rules determining the distribution of bioavailable nickel content of studied soils. In soils on limestone and on andesite the role of organic matter, in soil on andesite the role of clay minerals should be noted from this point of view.

Zinc

Zinc is readily adsorbed by clay minerals, carbonates, or hydrous oxides, while the precipitation is not a major mechanism for retention of Zn in soils because of high solubility of Zn compounds. In alkaline medium Zn hydrolyses, and its hydrolysed species are strongly adsorbed to soil surfaces. Zinc forms complexes with inorganic and organic ligands that will affect its adsorption reactions with the soil surface (McLean and Bledsoe, 1992).

Table 4. Correlation between the different element concentrations and some physico-chemical properties of the studied soils. A = (bio)available; M:M_A = correlation between the concentration of a given trace metal and its bioavailable amount.

Profile	pH	TOC	CM	Al	Fe	Mn	M:M _A
All							
Cu	-0,20	0,02	0,23	0,68	0,90	0,51	0,84
Cu _A	-0,39	0,13	0,10	0,45	0,67	0,70	0,84
Ni	0,2	-0,14	0,18	0,37	0,48	0,05	-0,11
Ni _A	0,19	0,08	-0,22	-0,30	-0,19	0,67	-0,11
Pb	-0,64	0,57	-0,27	0,29	0,33	0,64	0,71
Pb _A	-0,41	0,85	-0,54	-0,18	-0,25	0,31	0,71
Zn	-0,20	0,40	-0,02	0,83	0,73	0,22	0,30
Zn _A	-0,24	0,88	-0,60	-0,08	0,01	0,46	0,30
P09							
Cu	-0,88	0,28	0,26	0,80	0,85	0,72	0,70
Cu _A	-0,32	0,25	0,66	0,49	0,61	0,78	0,70
Ni	-0,34	-0,36	0,82	0,91	0,92	0,43	0,05
Ni _A	0,35	0,19	0,45	-0,08	-0,11	0,27	0,05
Pb	-0,90	0,77	-0,20	0,39	0,43	0,75	0,79
Pb _A	-0,48	0,99	-0,42	-0,20	-0,16	0,59	0,79
Zn	-0,86	0,33	0,40	0,86	0,90	0,82	0,11
Zn _A	-0,24	0,97	-0,37	-0,37	-0,33	0,52	0,11
P14							
Cu	-0,68	0,69	-0,60	0,41	0,28	-0,22	0,81
Cu _A	-0,56	1,00	-0,89	-0,28	-0,57	0,51	0,81
Ni	0,46	-0,75	0,56	-0,07	0,09	-0,07	0,34
Ni _A	0,85	-0,19	0,27	-0,54	-0,63	0,65	0,34
Pb	-0,60	0,68	-0,57	0,35	0,23	-0,22	0,74
Pb _A	-0,42	0,97	-0,87	-0,34	-0,68	0,63	0,74
Zn	-0,20	-0,13	0,15	0,76	0,75	-0,50	-0,24
Zn _A	-0,45	0,95	-0,85	-0,46	-0,73	0,68	-0,24
P15							
Cu	-0,36	-0,23	0,71	0,85	0,85	-0,17	0,40
Cu _A	-0,81	0,12	-0,02	0,61	0,66	0,25	0,40
Ni	0,41	-0,72	0,76	0,29	0,28	-0,71	-0,92
Ni _A	-0,80	0,73	-0,53	0,36	0,40	0,80	-0,92
Pb	-0,50	0,94	-0,76	-0,08	-0,06	0,91	0,98
Pb _A	-0,43	0,90	-0,80	-0,07	-0,04	0,86	0,98
Zn	-0,99	0,37	0,12	0,78	0,79	0,59	0,66
Zn _A	-0,62	0,87	-0,74	0,12	0,16	0,85	0,66
P16							
Cu	0,38	-0,44	0,41	0,60	0,90	-0,03	0,49
Cu _A	-0,07	0,05	0,23	-0,11	0,08	0,28	0,49
Ni	0,61	-0,31	0,25	0,46	0,79	0,16	-0,12
Ni _A	0,25	0,86	-0,96	-0,98	-0,98	0,93	-0,12
Pb	-0,24	0,89	-0,86	-0,77	-0,41	0,83	0,73
Pb _A	0,26	0,85	-0,96	-0,97	-0,99	0,92	0,73
Zn	0,33	-0,73	0,73	0,91	0,96	-0,47	-0,71
Zn _A	-0,45	0,97	-0,87	-0,79	-0,63	0,76	-0,71

The distribution of zinc is very similar to that of copper and in some cases to nickel. Its amount does not change in the soil profiles with depth, but in soil on siltstone zinc also accumulates in the B horizon following the distribution of Fe and Al. Similarly to Cu and Ni its amount increases in soil formed on calcareous rocks, and decreases in soil developed

on andesite as compared to the parent material.

Similarly to the copper, zinc correlates mostly with the distribution of Al and Fe well. The linear relation between these two metals is also good in some profiles (P09 and P16). The distribution of zinc in the carbonate containing profiles (P09 and P15) is very similar to the copper distribution.

Among the studied metals zinc is the least available: only 0-9 % of total zinc is available for plants. In general the highest amounts of soluble zinc (5-9% of total zinc) are found in the topsoil, while the subsoil contains negligible amount of soluble zinc. This suggests the role of the amount of soil organic matter in availability of zinc for plants, which is also shown by their good correlation. In most cases (P14, P15, and P16) the amount of available zinc decreases with increasing clay mineral content, showing the high affinity of zinc for clay minerals.

CONCLUSIONS

Distributions of total and soluble metal concentrations are generally similar in the studied profiles, significant differences were observed only in case of Zn. Their bioavailability differs from metal to metal, and the following sequence was observed: Pb > Cu > Ni > Zn.

Both the distributions of total and available amounts of Cu are uniform in all of studied profiles independent of variation of chemical and mineralogical composition of soils. Distribution of Pb in soils is determined by the distribution and amount of organic matter in soils. It is also supported by the fact that the extractability of Pb increases with the increasing organic matter content of soils. In case of Ni, neither the total nor the soluble amounts of this metal show any variations with depth. There is no general factor that would determine its distribution. Similarly, there is no general rule for the distribution of total Zn contents of soils either. On the other hand, the amount of bioavailable Zn increases with increasing organic matter content of soils.

Obvious effect on trace metal distribution was observed only in case of organic matter content of soils. It influences not only the bioavailable amount of Pb and Zn, but the total amount of Pb, as well. In the latter case the atmospheric fallout of heavy metals can play role in the decreased amount of lead in topsoil. The Cu and Zn contents show good correlation with total Al and Fe contents of soils, which may be due to the retention by amorphous oxides, but the characterization of this relation needs further studies. Stronger retention of trace metals by clay minerals is suggested in cases of Pb, Ni, and Zn by the good negative correlation of clay mineral and available metal contents of soils. These two components have contrary effects on heavy metal retention in soils.

The quality of bedrock influences the clay mineral composition of soils, thus it has an effect on heavy metal distribution in soils, which is, however, also influenced by other constituents independent of bedrock. The common effects of these factors form the actual distribution of heavy metals in soils.

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