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Distribution and sorption of potentially toxic metals in four forest soils from Hungary

Research Article

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Abstract: Metals of natural and anthropogenic origin behave differently in soils mostly due to their different mobility. In this study, sequential extractions and batch sorption experiments were performed to relate the fractionation of native Ni, Cu, Zn and Pb to the sorption properties of added metals in four soils with contrasting physiochemical characteristics. A significant effect due to sample composition on both the mobility and sorption characteristics of these metals was found. The efficiency of soil components in metal immobilization was in the order of carbonate > organic matter > swelling clay minerals. The partitioning of native metals together with the information gained through the sorption isotherms allows a deeper insight on the fate and behavior of metals in soils with various compositions.

Keywords: nickel • copper • zinc • lead • sequential extraction • batch sorption

1. Introduction

Heavy metals are natural components of soils. Their main source is rock mineral weathering and their concentrations remain mostly below toxic amounts in natural soils. However, increasing amounts of these metals are being incorporated to the soil through human activities associated with agriculture, industry and mining. The anthropogenic heavy metals are believed to be easily accumulated in the topsoil, resulting in potential problems, such as toxicity to living organisms [1]. Evaluation of the behavior of these metals in the soil-water-plant system is of great interest because of its possible effects on the food chain.

Transformation of metal-containing minerals during pedogenesis may affect the chemical speciation and bioavailability of metals. Soil chemical and physical properties like redox conditions, pH and water content affect the rate of transformation of metals in soil, and, along with the addition and depletion of salts, carbonates, clays and organic matter determine absolute and relative changes in heavy metal contents through soil profile. These multiple interaction processes result in complex patterns of element distribution in soil [2].

Total elemental contents provide little information on the mobility and bioavailability of the elements of interest. These properties of metals depend heavily on their physical and chemical forms. Sequential extraction, although operationally defined, can provide information about the association of heavy metals with geochemical phases in a soil and can therefore help to reveal the distribution of metals in fractions and to assess their mobility and toxicity. Generally, the exchangeable form is considered read-

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ily mobile and easily bioavailable, while the residual form is considered to be incorporated into the crystalline lattice of soil minerals and appears to be the most inactive. Others, such as the acid extractable, reducible or oxidizable fractions can be considered relatively active depending on the actual physicochemical properties of a soil [3].

The soil solution concentration, and hence the bioavailability or toxicity of these metals, are most likely controlled by sorption-desorption reactions on the surface of the soil colloidal materials. Batch equilibrium techniques are used to study the retention of metals in soils and the sorption data are described by isotherms. The analysis of isotherms provides information about the retention capacity and the strength by which the sorbate is held on to the soil. Owing to the complexity of the retention process of metals in soils, it is useful to combine sorption isotherms with sequential extraction procedures [4].

The aim of this paper is to relate the fractionation of native Ni, Cu, Zn and Pb to the sorption properties of added metals in four soils with contrasting physicochemical characteristics. The partitioning of native metals together with the information gained through the sorption isotherms allows a deeper insight into the fate and behavior of metals in soils with various compositions. Using concentrations characteristic of a serious metal pollution (up to 200 mg L^{-1} initial concentration in solutions) the behavior of metals in natural and polluted soils can be compared.

2. Materials and methods

The samples were collected from a Calcic (S1, S2, and S3) and a Haplic Luvisol (S4) profile, with silt loam and clay loam textures, respectively. Luvisols are among the most common soil types in Hungary, covering more than 10% of the country's area [5]. The Calcic Luvisol profile was developed on an Oligocene pelagic siltstone with significant mica (up to 30%) and carbonate (up to 20%) content. This rock underwent a low-degree of contact metamorphism associated with a Miocene andesite laccolite resulting in the partial transformation of mica to chlorite. The Haplic Luvisol profile is formed on a Miocene pelagic siltstone with significant mica (up to 30%) content but with no carbonate. The sampling sites are almost free of anthropogenic contamination; they are far from the main roads and industrial activity (Figure 1).

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

Soil	Horizon	Depth (cm)	Color	pH (H_2O)	CEC (cmol kg^{-1})	TOC (%)	Clay (%)	Carbonate (%)	Acid extractable Ca (mg kg^{-1})	Reducible Fe (mg kg^{-1})	Reducible Mn (mg kg^{-1})	Clay mineralogy
S1	A	0-5	10YR3/4	6.39	24.2	6.74	8	-	1426 ± 25 (20%)	2863 ± 163 (10%)	68 ± 1 (20%)	Vermiculite, Illite
S2	B_t	15-45	10YR5/8	6.85	22.8	0.39	15	-	477 ± 33 (12%)	4137 ± 151 (11%)	137 ± 4 (37%)	Vermiculite, Illite
S3	C_k	55-75	2.5YR6/4	8.08	12.4	<0.10	7	20*	43426 ± 3268 (45%)	2747 ± 124 (11%)	93 ± 4 (36%)	Chlorite/Vermiculite, Illite
S4	B_t	60-120	7.5YR5/2	4.84	38.7	0.15	45	-	313 ± 17 (5%)	2670 ± 22 (7%)	36 ± 1 (18%)	Montmorillonite, Illite

*According to the XRD analyses, the carbonate content of the sample S3 consists of calcite.

Values in parentheses for acid extractable Ca, as well as reducible Fe and Mn, indicate the contribution of the given fraction to the total concentration of element. The acid extractable and reducible element contents were determined by the sequential extraction method used in this study.

The air dried samples were passed through a 2 mm sieve. Some physico-chemical properties of the studied samples can be found in Table 1. The four studied samples were chosen according to their dominant components: soil organic matter, swelling clay minerals and Fe and Mn oxides. These components play significant roles in metal immobilization and show relatively high stability in soils, compared to other factors affecting metal sorption with intense temporal variability, such as pH or Eh [6]. The sample from the A horizon of the Calcic Luvisol profile is characterized by relatively high total organic carbon content (6.74%), when compared to other studied samples. Two samples are from the B_t horizons of the two profiles. One of them (S2) is characterized by relatively low clay content (15%) and clay mineralogy dominated by vermiculite, as well as by high reducible iron and manganese content, while the other one (S4) by high clay content (45%) and clay mineralogy dominated by montmorillonite. The fourth sample (S4) is from the C_k horizon of the Calcic Luvisol profile, which is characterized by calcite content of 20%.This is consistent with the high amount and ratio of Ca in the weak acid extractable fraction. Detailed characterization of the profiles can be found in the papers by Sipos [7] and Németh and Sipos [8].

Soil pH was measured in aqueous suspension by a Radelkis OP 211 analyzer. Total organic carbon content of the samples was determined by the Rock-Eval method (Delsi Oil Show Analyzer) [9]. Particle size distributions

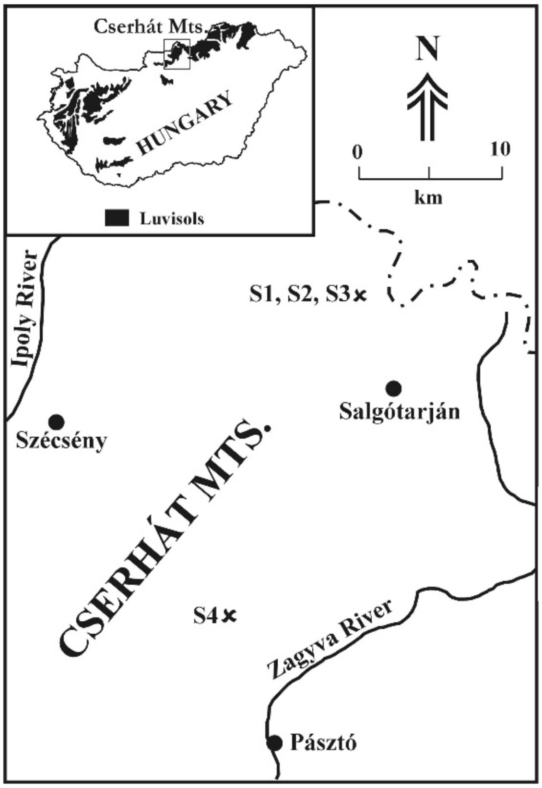

Figure 1. Geological sketch map showing the sampling sites.

of the samples were analyzed by the modified pipette method [10]. Mineralogical compositions of the samples were estimated by semi-quantitative phase analysis after the method by Bárdossy et al. [11] using X-ray diffractometric analyses (Philips PW 1710).

The sequential extraction method after Li et al. [12] was performed on the dried samples in a parallel set. The extractions were carried out progressively on an initial weight of 1.0 g soil in polypropylene centrifuge tubes of 50 ml. Five fractions were separated in five steps as follows: (1) exchangeable with 8 ml of 0.5 M $MgCl_2$; (2) weak acid soluble, extracted by 8 ml of 1M NaOAc adjusted to pH 5.0 with HOAc; (3) reducible, extracted by 20 ml of 0.04 M $NH_2{\cdot}OH{\cdot}HCl$ in 25% (v/v) HOAc; (4) oxidizable, extracted by 3 ml of 0.02 M HNO_3 and 5 ml of 30% H_2O_2 (adjusted to pH 2.0 with HNO_3), as well as by a second 3 ml aliquot of 30% H_2O_2 and 5 ml of 3.2 M NH_4OAc; and (5) residual, digested with 4 ml concentrated HNO_3, 3 ml perchloric acid and 15 ml hydrofluoric acid to dryness at 90°C with the remaining material then taken up in 5 ml of 5M HCl at 70°C. Following each extraction step, the mixtures were centrifuged at 3000 rpm for 20 min, and the solutions were separated from the solid material. The last step of the sequential extraction procedure was done also on the initial soil samples to determine their total metal content. The concentration of Ni, Cu, Zn, Pb as well as that of Ca, Mn and Fe were analyzed using ICP-AES method (Jobin Yvon Ultima 2 sequential ICP) in the solutions. Comparing the sum of metal extracted from each fraction to their total content the recoveries of metals were 90-101% for Ni, 88-103% for Cu, 95-104% for Zn. The total lead concentrations were significantly lower than that derived from the sum of the fractions (recoveries were between 150 and 166%) probably due to the re-adsorption of lead during the total extraction [13]. Mobility factor for the studied metals were calculated from the results of the sequential extraction studies according to Kabala and Singh [14] as follows:

$$\mathrm{MF} = \frac{\mathrm{F1} + \mathrm{F2}}{\mathrm{F1} + \mathrm{F2} + \mathrm{F3} + \mathrm{F4} + \mathrm{F5}} \times 100,$$

where F1, F2...F5 are the concentration of the given metal in the different fractions of the sequential extraction used.

Batch adsorption experiments were carried out in polypropylene centrifuge tubes of 50 ml by mixing 200 mg sample with a 20 ml solution containing various concentrations of the studied metals. Metals were added to the solutions in the form of nitrate salts. The highest added metal concentrations in solutions were 200 mg L^{-1} in the single element experiments. Additionally, the following dilution rates of these solutions with distilled water were used: 0.75, 0.5, 0.4, 0.25, and 0.1. These values seem to be very high with respect to the natural metal content of a soil, but they may occur in case of serious metal pollution. The samples mixed with the solutions of different metal concentrations were shaken lengthwise for 48 hours at 25°C. Then they were separated by centrifugation at 3000 rpm for 20 minutes. Their concentrations in the equilibrium solutions were analyzed by AAS method (Perkin-Elmer AAnalyst 300). The relative standard deviations for the studied metals were as follows in the duplicate samples: 1.6% for Pb, 1.8% for Ni, 2.8% for Cu and 3.0% for Zn.

The linear, Langmuir and Freundlich isotherm equations were used to describe the sorption of the metals from the solution onto the studied soil samples [15]. The relative percentage change or sorption intensity (SI) was also used to compare the metal sorption capacity of the samples [16]. It can be calculated by taking the difference between the initial and equilibrium metal concentrations, then dividing this difference by the initial metal concentration, and then expressing this as a percentage by multiplying by 100 for each initial concentration used. This parameter was calculated by summarizing the individual SI values for each initial concentration used as follows:

$$\mathrm{SI}_{\Sigma} = \frac{\sum (\mathrm{C_i} - \mathrm{C_e})}{\sum \mathrm{C_i}} \cdot 100,$$

where C_i is the initial and C_e is the equilibrium concentration of a given metal in solution.

3. Results and discussion

3.1. Fractionation of native metals in the soil samples

Table 2 shows the total concentrations of Ni, Cu, Zn and Pb in the studied soils and their amounts extracted from the five fractions of the sequential extraction. The total concentration of metals was within the range of the most frequent values for natural soils [17]. The samples free of carbonate show slightly higher metal concentrations than the sample with 20% carbonate content. Pedogenic accumulation of carbonate minerals in this latter sample resulted in relatively lower metal amounts.

The sequential extraction showed the predominance of metals associated with the residual fraction: 74-82% of the total Ni, 77-93% of the total Cu, 74-88% of the total Zn, and 43-72% of the total Pb were found in this fraction (Figure 2). Metal concentrations in the exchangeable fractions were lower than the detection limits of the analytical technique. Similar results were reported by other authors in uncontaminated soils [4, 18].

Table 2. Fractionation of metals in the studied soils.

Metal	Soil	(1) Exchangeable (EX)		(2) Acid extractable (AE)		(3) Reducible (RED)		(4) Oxidizable (OX)		(5) Residual (RES)		Sum of fractions	Total (TOT)
		(mg kg^{-1})[*]	(%)[**]	(mg kg^{-1})	(%)	(mg kg^{-1})	(%)	(mg kg^{-1})	(%)	(mg kg^{-1})	(%)	(mg kg^{-1})	(mg kg^{-1})
Ni	S1	<0.06	<0.2	0.54 ± 0.07	2	3.0 ± 0.4	10	4.3 ± 0.5	14	23 ± 0.4	75	31 ± 1.4	31 ± 1
	S2	<0.06	<0.1	2.0 ± 0.3	4	5.9 ± 0.4	13	1.9 ± 0.3	4	36 ± 1.7	78	45 ± 2.6	47 ± 0.2
	S3	<0.06	<0.2	1.1 ± 0.1	4	4.3 ± 0.2	16	1.5 ± 0.3	6	20 ± 0.6	74	27 ± 1.3	27 ± 0.4
	S4	<0.06	<0.2	0.76 ± 0.10	3	2.6 ± 0.1	9	1.7 ± 0.3	6	22 ± 0.1	81	27 ± 0.7	30 ± 0.3
Cu	S1	<0.01	<0.08	0.07 ± 0.11	0.5	<0.044	<0.3	0.8 ± 0.01	6	12 ± 0.1	93	13 ± 0.3	14 ± 0.1
	S2	<0.01	<0.06	0.07 ± 0.08	0.4	0.74 ± 0.13	4	0.7 ± 0.5	4	15 ± 2.7	91	17 ± 3.4	19 ± 0.2
	S3	<0.01	<0.08	0.16 ± 0.23	1	0.39 ± 0.11	3	1.0 ± 1.0	8	11 ± 0.1	87	12 ± 1.5	12 ± 0.1
	S4	<0.01	<0.07	0.26 ± 0.12	2	0.86 ± 0.07	6	2.2 ± 1.2	15	11 ± 0.3	77	14 ± 1.7	15 ± 0.1
Zn	S1	<0.02	<0.02	1.9 ± 0.7	2	13 ± 0.4	17	5.4 ± 0.3	7	60 ± 2.3	74	81 ± 3.8	83 ± 0.4
	S2	<0.02	<0.02	0.25 ± 0.29	0.3	8.4 ± 0.3	10	1.7 ± 0.5	2	73 ± 5.4	87	83 ± 6.5	87 ± 0.4
	S3	<0.02	<0.04	0.14 ± 0.24	0.3	7.1 ± 0.1	13	1.2 ± 0.1	2	46 ± 1.0	85	55 ± 1.4	53 ± 0.5
	S4	<0.02	<0.02	0.03 ± 0.05	0.03	6.6 ± 0.5	8	2.9 ± 0.3	4	72 ± 3.1	88	81 ± 3.8	82 ± 1
Pb	S1	<0.13	<0.4	3.9 ± 0.3	11	9.2 ± 0.5	27	6.4 ± 0.3	19	15 ± 1.7	43	34 ± 2.9	23 ± 1
	S2	<0.13	<0.5	0.56 ± 0.20	2	6.5 ± 0.2	25	1.9 ± 0.1	7	17 ± 3.0	65	26 ± 3.5	17 ± 2
	S3	<0.13	<0.8	<0.28	<2	3.7 ± 0.2	23	0.6 ± 0.01	4	11 ± 0.3	70	15 ± 0.5	10 ± 1
	S4	<0.13	<0.5	1.2 ± 0.2	4	4.2 ± 0.1	15	2.4 ± 0.1	9	19 ± 0.1	71	27 ± 0.7	16 ± 0.2

[*] Concentrations of metals in the given fraction.

[**] Contribution of the given fraction to the sum of fractions.

The second most important fraction for Ni is the reducible fraction, suggesting an association with oxide phases of soils after its mobilization during rock mineral weathering. Its contribution to the total Ni content of the studied soils is between 9 and 16%. Many studies have found a close relation between soil Fe and Ni, suggesting that Fe oxides are important sinks for Ni in soils [19, 20]. The role of the oxidizable fraction is only important for Ni in the sample with the highest total organic carbon content (S1). Soils often show an accumulation of Ni in surface horizons due to the high affinity of this metal to organic matter [21]. However, in other cases this fraction, along with the acid extractable fraction, is negligible for this metal in the studied soils. The mobility factor of Ni is generally the highest among the studied metals (MF = 1.7-4.4) except for the sample with the highest TOC content (S1), where a relatively large amount of Ni was found in the oxidizable fraction. According to de Melo et al. [22] nickel tends to be associated with the most stable fractions of the soil organic matter in soils treated with sewage sludge, resulting in a low mobility for this metal.

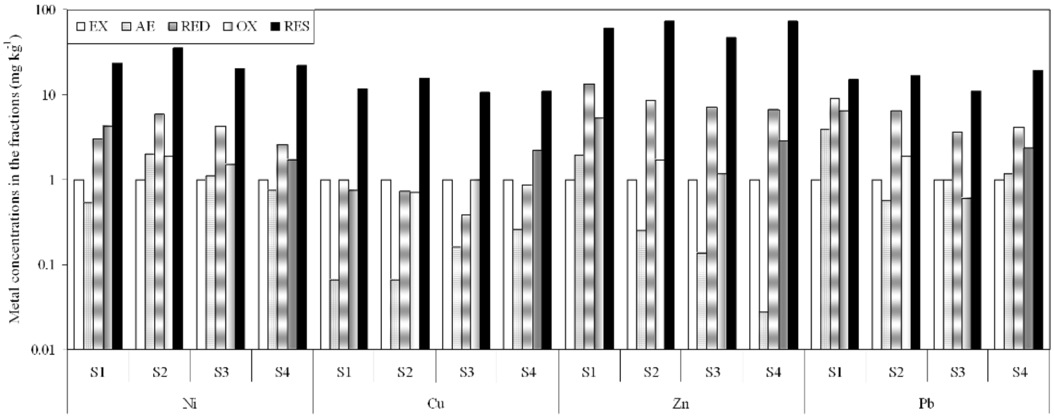

Figure 2. Fractionation of Ni, Cu, Zn and Pb in the studied samples.

In most of the samples the importance of acid extractable, reducible and oxidizable fractions is negligible for Cu. Their contribution to the total Cu content is generally well below 10%. The only exception is the oxidizable fraction in the sample containing high amount of montmorillonite (S4) where 15% of total Cu is bound to this fraction. Despite the high amount of clay minerals and the relatively low TOC content, the mobilized Cu was retained by the organic matter of this sample, showing the higher affinity of this metal to soil organic matter than to montmorillonite. Many authors have found a higher sorption capacity of humic substances for metals relative to inorganic soil components [23, 24]. Being a mostly negligible fraction in the studied samples, the oxidizable one is still the second most important one for this metal. According to the mobility factors, copper shows the lowest mobility among the studied metals (MF = 0.4-1.8). Copper is known as a metal with low mobility in natural soils [25, 26].

Similarly to Ni, relatively high amount of zinc can be found in the reducible fraction (8-17%). The role of the acid extractable and oxidizable fractions is negligible for Zn in the studied samples. The significant role of the Fe and Mn oxide (e.g. reducible) fraction for Zn was found both in natural [27] and polluted soils [28]. The most intense mobilization for Zn was found in the sample with the highest TOC (S1), where the labile zinc pool consist mostly of the reducible (17% of the total Zn) and partly of the oxidizable (7% of the total Zn) fractions. In all other samples, Zn shows a very low mobility (MF = 0-0.3).

Lead shows the highest mobilization among the studied metals in the samples. High amounts of lead can be bound to the reducible fraction. Its contribution to the total lead content of the samples is between 15 and 27%. Teutsch et al. [29] found that lead is probably adsorbed and coprecipitated with Fe oxides and hydrous oxides. The role of the oxidizable fraction is also important for this metal in the sample with the highest TOC content: 19% of the total Pb can be bound to it. Among the metals studied, lead has the highest affinity for the soil organic matter [30]. Additionally, the acid extractable Pb content of this sample is also significant (11% of the total Pb). Generally, the role of acid extractable, reducible and oxidizable fractions was more significant for Pb than for other studied metals. This is also shown by the high mobility factors for the lead, which are up to 11 in the sample S1, but also high for sample S4 (MF = 4.4).

The mobility factors of Ni, Cu, Zn and Pb show high variability among the studied samples. Generally, Pb and Ni exhibit relatively higher mobility, while Cu and Zn show lower mobility. This result is similar to those reported by different heavy metal mobility studies [31–33] except in the case of Pb, which is more mobile in these soils than expected. The unexpected high lability of Pb as compared to other metals suggests the presence of different (natural or anthropogenic) lead sources [34]. However, Pb in the sample containing carbonate (S3) is characterized by the lowest mobility among the studied metals, which may be due to the alkaline conditions, where Pb shows generally almost complete retention [35]. Additionally, the mobility of Zn is one of the highest in the sample rich in organic matter (S1), which can not be related to the high organic matter content of this sample, as labile Zn can be bound mostly to the reducible fraction also in this sample.

3.2. Sorption of the added metals on the soil samples

The results of the sorption experiments are summarized in Table 3. In most of the cases the Langmuir adsorption isotherm showed the best fit for samples and metals studied. The R^2 values always exceeded 0.79, but generally they were above 0.98. Due to these excellent fits, the parameters derived from the Langmuir isotherms were used to compare the sorption characteristics of metals and samples studied. Exceptions are the Pb sorption on the sample with the highest TOC content (S1), and Cu and Pb sorption on the sample containing carbonate (S3). In these cases, the sorption of Pb and Cu can be described most effectively by the linear isotherm.

Nickel shows the highest affinity for the sample containing carbonate (S3). Nearly two times greater retention was found on this sample compared to the other ones (Q_{max} = 250 mmol kg^{-1} on the sample S3, while between 115 and 159 mmol kg^{-1} on the other three samples).

Table 3. Results of the sorption experiments. Parameters are given only in cases where $R^2 > 0.50$.

Metal	Soil	pH_{eq}		SI_{joint}	Linear			Langmuir				Freundlich	
		min	max	(%)	K_d	R^2	Isotherm type	Q_{max} (mmol kg^{-1})	(mg kg^{-1})	b (L $mmol^{-1}$)	R^2	K_F	R^2
Ni	S1	6.14	7.07	52	-	-	S2	159	9 317	3	0.95	28	0.87
	S2	5.18	5.90	42	-	-	S2	120	7 072	2	0.79	18	0.67
	S3	7.12	8.18	88	-	-	H1/H2	250	14 675	133	1.00	22	1.00
	S4	5.83	6.00	44	-	-	L2	115	6 747	4	0.99	20	0.99
Cu	S1	4.98	7.01	82	-	-	L2	213	13 520	24	1.00	35	0.99
	S2	4.57	5.66	48	-	-	L2	122	7 750	4	0.98	19	0.94
	S3	7.51	8.27	100	72 976	0.88	C	370	23 536	270	0.84	76	0.91
	S4	4.50	5.34	51	-	-	L2	135	8 587	4	0.99	24	0.97
Zn	S1	4.59	5.11	24	-	-	L2	48	3 114	6	0.99	7	0.95
	S2	5.23	6.02	40	-	-	L1	93	6 055	4	0.99	16	0.99
	S3	6.85	7.83	76	-	-	L1	200	13 078	13	0.98	25	0.94
	S4	4.45	4.82	44	-	-	L1	109	7 108	3	0.99	20	0.99
Pb	S1	5.89	6.60	100	-	1.00	C	-	-	-	-	-	-
	S2	4.82	6.88	94	-	-	H1	83	17 267	400	1.00	11	0.94
	S3	7.48	8.04	100	40 041	0.68	C	-	-	-	-	-	-
	S4	5.18	5.7	93	-	-	L1	104	21 583	48	0.99	20	0.98

In this case, Ni exhibits an H1/H2 type isotherm (Figure 3). The H-type isotherm indicates a very strong adsorbate-adsorbent interaction (i.e. usually chemisorption), and the H1/H2 subtype suggests that the theoretical monolayer was close to completion [36]. The sample characterized by the highest TOC content (S1) showed the second highest affinity for Ni with 159 mmol kg^{-1} maximal sorption, followed by similar maximum sorption values for the samples containing vermiculite (S2 Q_{max} = 120 mmol kg^{-1}) and montmorillonite (S4 Q_{max} = 115 mmol kg^{-1}). The samples S1 and S2 exhibit an S2-type isotherm, while sample S4 shows an L2-type isotherm (Figure 3). The S-class isotherm suggests cooperative adsorption, which operates if adsorbate-adsorbate interaction is stronger than adsorbate-adsorbent interaction. In this case, the clusters of adsorbate ions at the surface are favored because they bound more strongly with one another than with the surface. In contrast, the L-type isotherm reflects a relatively high affinity between the adsorbate and the adsorbent, and it usually indicates chemisorption. Subtype 2 suggests that the theoretical monolayer has been completed in all these cases [36]. Consequently, despite the lowest maximum sorption of Ni for the sample containing montmorillonite (S4), the affinity of this metal is higher for this sample relative to samples S1 and S2, which is also supported by the differences in b values representing the Langmuir bonding term related to the adsorption energy (Table 3).

Copper generally shows the highest affinity towards the studied samples. This is also suggested by the shapes of the isotherms, which are C-type for the sample containing carbonate (S3), and L2-type for all the carbonate-free samples (Figure 3). The C-type isotherm, or constant partitioning isotherm, suggests a constant relative affinity of the adsorbate ions for the adsorbent [36]. The complete retention of Cu on this sample (SI_{joint} = 100%) also suggests its high immobilization capacity for this metal. Using analytical electron microscopy analyses, Sipos et al. [37] found that Cu shows very high sorption in this sample, even in the presence of competing metals such as Pb and Zn. Their results also show that some of the Cu may have also been precipitated as carbonate. The variations of maximum sorption values among the studied samples for Cu show similar trends to that observed for Ni. The highest Cu immobilization was found in the sample containing carbonate (S3) (Q_{max} = 370 mmol kg^{-1}), followed by the sample characterized by the highest TOC content (S1) (Q_{max} = 213 mmol kg^{-1}). The samples containing vermiculite (S2) and montmorillonite (S4) show similar sorption capacities for Cu, their Q_{max} values are 122 and 135 mmol kg^{-1}, respectively.

Zinc shows a slightly different sorption behavior than Ni and Cu. Similarly to the other metals studied, it exhibits the highest affinity towards the sample containing carbonate (S3) with a Q_{max} value of 200 mmol kg^{-1}. However, the sample rich in TOC (S1) immobilized the lowest Zn amounts among the samples studied (Q_{max} = 48 mmol kg^{-1}). Again, samples containing vermiculite (S2) and montmorillonite (S4) show similar Zn sorption capacities, 93 and 109 mmol kg^{-1}, respectively. The shapes of the Zn isotherms for the different samples suggest a relatively high affinity and the lack of completion of the theoretical monolayer (L1-type isotherms), except for the sample with lowest affinity for Zn (S1) where the monolayer has been completed (L2-type isotherm) (Figure 3).

Lead exhibits a unique sorption behavior among the studied metals. It shows very high affinity for all of the studied samples. In the samples containing carbonate (S3) and the largest amount of TOC (S1), all of the lead present in the initial solutions was immobilized (their SI_{joint} values are 100%). Sipos et al. [37] found the precipitation of Pb-carbonate in sample S3 using X-ray diffractometric analyses. It is likely that this process contributed to the high immobilization of Pb in this case as well.

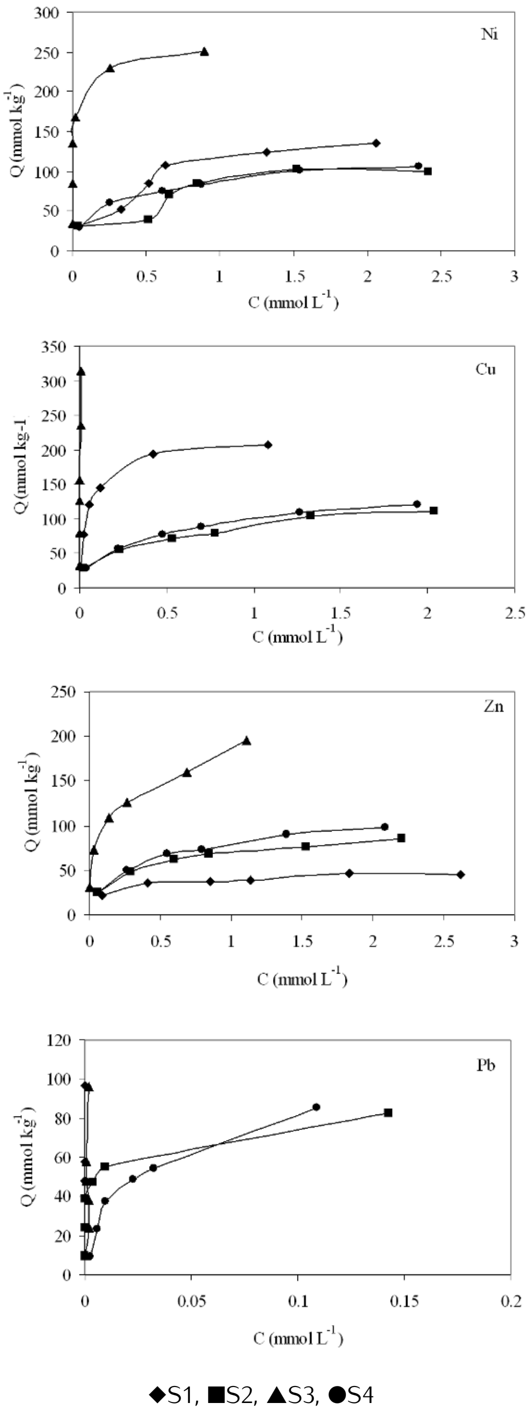

Figure 3. Sorption isotherms of Ni, Cu, Zn and Pb on the studied sample.

Moreover, the sorption intensity values for the other studied samples also suggest almost complete retention, as these values are 94 and 93% for the samples containing vermiculite (S2) and montmorillonite (S4), respectively. In contrast, in these latter two samples, the Q_{max} values for Pb are the lowest among the studied samples (83 and 104 mmol kg^{-1}, respectively). The apparently low sorption capacity of these samples for lead is due to the large differences between the initial molar concentrations of Pb and the other studied metals, which are between 3.05 and 3.41 mmol L^{-1} for Ni, Cu and Zn, while 0.97 mmol L^{-1} for Pb.

By far, the highest metal amounts were retained by the sample containing carbonate (S3) (up to 4 times more than by the other samples). Copper and Pb show complete retention in this sample (their joint sorption intensity is 100%), while 88 and 76% of added nickel and zinc is immobilized on this sample, respectively. Fontes et al. [38] found similar sorption behaviour for metals in limed soil samples. Their results indicated that the presence of carbonates in the soil created new sorption sites and also favoured the precipitation of metals, such as Cu, Pb and Zn. Metal precipitation in soils can occur at alkaline conditions, relatively high metal concentrations, and low metal solubility or also in the case of small number of specific adsorption sites [39]. In this sample, the presence of carbonates led to an elevated pH (soil pH = 8.41), and the equilibrium pH values were also in the neutral and slightly alkaline range (lowest pH_{eq} values are between 6.85 and 7.48). According to Brookins [40] these conditions may favor the precipitation of these metals as carbonates. Besides the very high adsorption, precipitation may have played also role in the immobilization of Cu and Pb in this sample.

Among the samples free of carbonate, Ni, Cu and Pb showed higher affinity towards the sample rich in TOC (S1) than for the other carbonate free samples (S2 and S4). In contrast, Zn exhibited higher affinity towards the samples characterized by vermiculite and montmorillonite than to the sample S1. As the sample S1 can be characterized by a relatively high total organic carbon content (TOC = 6.74%), these results are in good agreement with those on a metal affinity sequence towards humic substances published by several authors [41, 42]. This trend follows the Irving-Williams series, which describes the order of stability of organic-metal complexes. The order of this series arises in part from a decrease in ionic size and in part from ligand field effects [43].

The samples containing vermiculite and montmorillonite are characterized by the lowest sorption capacity among the samples studied. However, their maximum metal sorption capacity is still considerable (they are able to immobilize up to 8,000 mg kg^{-1} Ni, Cu, and Zn, as well as and 21,000 mg kg^{-1} Pb). Generally, the sample characterized by montmorillonite retained slightly higher metal amounts than that containing vermiculite as this sample contains higher amount of clay as well (45% clay for S4 and 15% clay for S2). According to Abollino et al. [44] the order of affinity of the studied metals for montmorillonite and vermiculite are similar to that found in this study in a wide pH range (between 2.5 and 8.0). They showed that the adsorption of divalent metal ions on these phases increases with decreasing facility of cations to hydrolyze and with increasing atomic weight of a metal ion. However, the presence of pedogenic iron oxide phases may also influence the sorption capacity of these samples (see Table 1). Many studies showed that the iron-oxide phases in soils may significantly contribute to the adsorption of these metals, especially for Pb and Zn [45]. Analytical electron microscopy analyses of Sipos et al. [37] showed that the association of iron oxides and clay minerals is more characteristic of the sample containing montmorillonite (S4) resulting in an enhancement of sorption capacity for these phases.

4. Conclusions

Sample composition strongly influenced both the mobility and sorption of the studied metals. The soil sample with the highest amount of carbonate is able to effectively immobilize a serious metal pollution due to alkaline conditions. These conditions also mostly result in low mobility for native metals, except for Ni, which is more mobile in this environment when compared to the other studied metals. The second most significant immobilization was found for the sample with high total organic carbon, although in this sample, Zn showed low retention and high mobility. Samples with a considerable amount of swelling clay minerals have lower sorption capacities relative to samples with high carbonate and organic matter content. However, their immobilization capacity is still considerable and native metals also show low mobility in these samples. The most important labile fraction for the studied metals is the reducible one, suggesting a significant role for Fe-oxides in the metal distribution of forest soils. The combined use of metal fractionation and sorption results in a better understanding of soil-metal interaction.

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