

Assessment of Lead Sorption by Acid Agroforest Soils

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Abstract

Agroforest soil samples were collected at two depths (0-20 and 20-40 cm) near the Glogow Copper Plant (Poland). Adsorption parameters and isotherms were obtained by fitting the data to the Freundlich equation. The K_F values of soil samples from the depth 0-20 cm were lower (from 32.1 to 45.4 dm³/kg) than those calculated for the soils No 6 and 7, i.e. 48.7 and 51.4 dm³/kg, respectively. The multiple regression analysis revealed that pH, clay content and additionally organic matter content most influenced the magnitude of K_F values. Buffering indices gave a best estimation of the adsorption isotherm made on the basis of K_F and n values only. The lack of high correlation coefficients between K_F and soil properties as well as "total Pb" and the latter ones may be attributed first to the specificity of agroforest soils and second to their presumable anthropogenic origin.

Keywords: agroforest soils, Pb sorption, Freundlich equation, buffering indices

Introduction

The behavior of heavy metals in the terrestrial environment has gained greater attention during the last two decades due to the increasing burden of metals on this environment from mainly anthropogenic activities such as dumping of industrial effluents as well as agricultural applications of sewage sludge [1]. Heavy metals fate is primarily governed by retention and release reactions of the solute with the soil matrix. In acid soils being naturally characterized by an enhanced metals solubility and activity, there is a great concern for assessing potential metals mobility. This may be the case of forest soils, generally low in organic matter content and with a real tendency for acidification. The formation of organo-metal complexes in the presence of organic substances may increase the partitioning of metals towards the solid phase. Components that partition more strongly to the solid phase exhibit low mobility in soils while those that partition more strongly to the liquid phase have greater mobility and may ultimately lead to a severe contamination of soil deeper layers [11].

There is an extensive body of reports describing re.ten-

tion (adsorption) of various metals by soils [4, 16, 18, 22]. These concern in most cases the retention of a single or few metals by a single or few non forest soils. Several equations are used or even modified for assessing the affinity of a soil system for a metal or nonmetal retention [7, 15, 16, 17]. The difficulty remains on the adequate choice of a given equation for a best interpretation of sorption parameters. Some correction of the original Freundlich isotherm equation to take into account the amount of phosphorus already present in the soil (D) was earlier reported by Fitter and Sutton [5]. Such possibilities for the description of phosphate sorption were also reported by Nychas [13] and Assimakopoulos et al. [2] designating q as the amount of phosphorus already present in the soil. Another transformation (extended Freundlich equation) for assessing the curve shape by BC^{-D} (where B represents the commonly reported n ; C - equilibrium concentration and D - amount of phosphorus already present in the soil) were developed by Sibbesen [17]. In a recent work Yang [22] had widely detailed the statistical and mechanical application of the original Freundlich equation.

The objective of the current study was to evaluate lead adsorption parameters in acid agroforest soils and to relate these parameters to basic properties of the soils.

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Materials and Methods

Soil samples used in this work were made available by the Institute of Dendrology of the Polish Academy of Sciences (PAN, Kornik near Poznań - Poland). They were collected from agroforest soils near the Glogow Copper Plant (Poland). Soil particle size was determined by the hydrometer method, organic carbon by the method of Tiurin [19] and soil pH in 0.01M CaCl₂ suspension [14] using a glass electrode. Cation exchange capacity (CEC) by the Mehlich₈₂ method modified by Kocialkowski and Ratajczak [8]. Free iron and manganese oxides were estimated according to McLaren and Crawford [10] and the "total Pb" was extracted by heating appropriate soil samples for two hours in 2M HNO₃ at soil to solution ratio 1:10 [6].

Adsorption Studies

Different Pb concentrations of 0.2, 0.4, 0.6, 1.0, 1.2, 1.6, 2.0, 2.4, and 2.8 mmol/dm³ were prepared by dissolving appropriate amounts of Pb(NO₃)₂ in 0.01M Ca(NO₃)₂ as a background electrolyte. These solutions were added to soils at 1:20 soil/solution ratios in a series of polyethylene centrifuge tubes and shaken for two hours. They were allowed to equilibrate over the night and filtered. The concentrations of Pb in 2M HNO₃ and in the equilibrium concentration (C_e) were determined by AAS method (Atomic Absorption Spectrophotometry, Varian Spectra 250 plus). The solid-phase Pb was calculated as the difference between initial Pb concentration (C_i) and that remaining in the solution after equilibration. The nonlinear corrected Freundlich adsorption equation used for this purpose was:

$$S + S_0 = K_F C_e^n \quad (1)$$

$$S = K_F C_e^n - S_0 \quad (2)$$

(for abbreviation description see appendix)

Table 1. Physical and chemical properties of the studied soils.

Soil	Sand	Silt	Clay	pH (0.01M CaCl ₂)	CEC* (cmol _c /kg)	C _{org} ** (g/kg)	Free oxides***		Pb (mg/kg)
	(g/kg)						Fe	Mn	
							(mg/kg)		
Layer: 0-20 cm									
1	485.0	475.0	40.0	4.55	3.80	7.80	1335.0	108.0	111.4
2	430.0	470.0	95.0	4.65	4.50	8.80	1200.0	161.0	131.2
3	660.0	310.0	30.0	4.70	4.50	9.00	1550.0	99.0	198.0
4	560.0	380.0	60.0	4.65	5.36	9.60	2390.0	227.0	211.2
5	680.0	280.0	40.0	4.85	4.50	7.80	1860.0	126.0	228.0
Layer: 20-40 cm									
6	600.0	345.0	55.0	5.05	4.50	8.40	1715.0	144.0	23.8
7	675.0	275.0	50.0	5.50	3.00	6.60	1275.0	95.0	66.7

* - Cation exchange capacity, at pH 8.2 (Mehlich₈₂)

** - Organic carbon

*** - According to McLaren and Crawford [9]

(For more details, see Materials and Methods)

and its first derivative equation giving the slope value of the tangent at any point was suggested by Assimakopoulos et al. [2] as:

$$\frac{dS}{dC_e} = K_F n C_e^{n-1} \quad (3)$$

The S value for each measurement was calculated as follows:

$$S = (C_i - C_e) \cdot V / W + S_0 \quad (4)$$

Results and Discussion

The soil physical and chemical properties listed in Table 1 show some characteristics of forest soils, i.e. sandy soils with a tendency for acidification and additionally a relative weak buffering capacity that may be attributed probably to the relatively low organic matter content. The cation exchange capacity (CEC) was comprised between 3.80 and 5.36 cmol_c/kg for soil samples collected at the depth 0-20 cm, whereas for the subsoil ones (20-40 cm) the CEC values were 4.50 and 3.00 cmol_c/kg for soil 6 and soil 7, respectively. The fate of heavy metals is controlled by their solubility being partly related to the leaching of basic cations and the presence of proton-generating iron, aluminum and manganese oxides in soils [9]. In such cases metal and Pb sorption may be strongly influenced by soil acidification.

Lead Adsorption by the Soil

Freundlich adsorption parameters and the values of the buffering indices are listed in Table 2. As can be seen, the values of the parameter K_F were not constant, but depended on the type of investigated soil. For the upper layers (0-20 cm) they varied from 32.1 to 45.4 dm³/kg, whereas for the

Table 2. Freundlich adsorption parameters and some buffering indices (BI) for the studied soils.

Soil	Parameters			BI values at C_i		
	K_F	n	r^*	0.2	1.2	2.8
Layer: 0-20 cm						
1	32.1	0.415	0.991	336.74	69.06	21.82
2	38.6	0.385	0.980	564.71	92.15	14.60
3	45.4	0.511	0.970	210.50	91.83	38.75
4	41.0	0.399	0.989	451.80	99.01	32.45
5	40.9	0.481	0.982	195.33	72.97	32.50
Layer: 20-40 cm						
6	48.7	0.399	0.925	813.86	178.36	45.81
7	51.4	0.468	0.942	447.19	116.97	46.56

For more details, see "Materials and Methods"

* - significant at $P < 0.001$ at least.

subsoil samples the values were found to be relatively high, 48.7 and 51.4 for soils 6 and 7 respectively. The Freundlich adsorption (K) values obtained by Suduan et al. [18] were markedly low in comparison to those reported herein. One of the limiting factors, and simultaneously influencing the decrease of the K_F values for both soil layers, was low organic matter content. Soil parameters such as pH and clay content may be considered as stable, so the focus was strongly set on organic matter content as shown by the use of the multiple regression equations ($P < 0.05$):

$$K_F = 19.81 \text{ pH} - 0.012 \text{ Clay} + 3.81 \text{ CEC} - 65.0; \\ R^2 = 70\% \quad (5)$$

The replacement of CEC by C_{org} notably increased the value of the coefficient of determination, R^2 by about 20%:

$$K_F = 22.77 \text{ pH} - 0.015 \text{ Clay} + 4.21 C_{\text{org}} - 96.0; \\ R^2 = 90\% \quad (6)$$

The next pattern used in this work for testing the affinity of the agroforest soils to adsorb Pb was the classification of soil samples based on so-called "total Pb" content (Table 2). Results of adsorption isotherms are graphically presented in Figures 1a (layer 0-20 cm) and 1b (layer 20-40 cm). It was expected that in such sandy and acidic soils characterized generally by low buffering properties the maximal Pb adsorption point could be reached at relatively lower C_i levels. This expectation was not fully met even at the highest Pb concentration (2.8 mmol/dm³) as illustrated on all figures, irrespective of sampling depth. Nevertheless, for most adsorption isotherms the inflexion of the isotherms started at equilibrium concentration (C_e) below 0.05 mmol/dm³. In terms of metal retention, these soils undoubtedly partition more strongly to the liquid phase, hence increasing metal mobility and ultimately leading to a phytocontamination as well as a contamination of deeper soil layers. The course of the isotherms pointed out by Narwal et al. [12] were very steep for all metals, which was probably attributable to the high organic carbon content of the soils being tested (24.2 to 342.0 g C/kg) and the CEC: 12.5 - 93.0 cmol/kg. On the other hand the shape of the iso-

therms (less steep) herein reported are similar to those illustrated by Salim et al. [16] for soil samples with CEC varying from 10.0 to 17.5 cmol/kg, reflecting a relatively low organic matter content. The correction parameter (S_o) previously introduced to consider the amount of Pb already present in the soil did not significantly exert a noticeable influence on the whole adsorption processes between surface soil (high Pb content) and subsoils (low Pb content). Nevertheless, some slight differences in the values of the slopes were observed, of which the lowest was for soil 1 (3.91) and the highest for soil 3 (5.78).

Another explanation of the similarity in the curve shapes may be derived from the competitive rate of Ca^{2+} (used as a background electrolyte) for the adsorption sites. In terms of coulombic attraction Ca^{2+} can equally compete with Pb^{2+} for surface sites. However, in this case there is a possibility that Ca^{2+} can also effectively compete with Pb^{2+} in terms of chemical bonding. Such eventuality has to be taken into account especially when providing sorption studies with light and sandy soils, which was clearly presented by Boekhold et al. [3].

Lead Buffering Indices

The values of the buffering indices (BI) were calculated from the first derivation of the corrected Freundlich equation (3). Table 2 lists some BI values for selected three initial Pb concentrations (i.e. $C_i = 0.2, 1.2,$ and 2.8 mmol/dm³). The assessment of Pb sorption by the mean of these indices seems to be more practical than the use of the dimensionless Freundlich parameter n and K_F . This is mainly attributed to the fact that n as well as K_F covers the whole range of Pb solution concentrations used, whereas buffering indices may reveal step by step the changes in Pb adsorption. To avoid the direct influence of Pb already in soil on the adsorption of Pb from the initial concentrations, it was found convincing to plot BI values versus equilibrium concentration (C_e). A confirmation of this assumption was provided by Figures 2a and 2b representing the surface and subsoil samples, respectively. In terms of complex soil saturation it was found that soils 3, 5, and 7 were

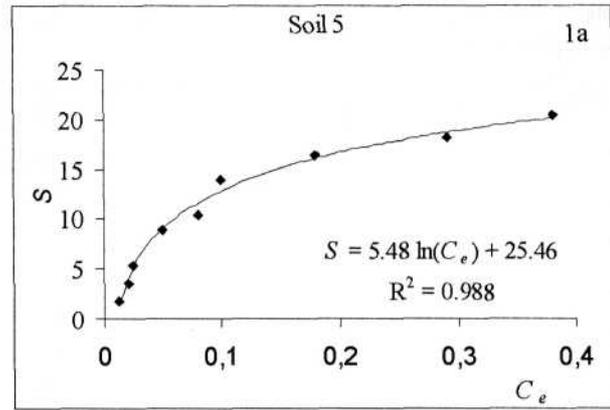
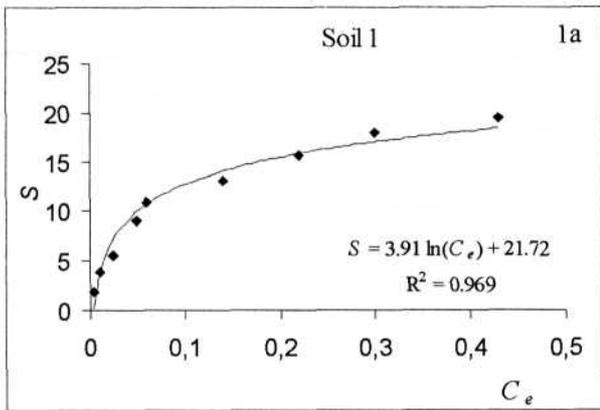


Fig. 1a. Representative Pb adsorption isotherms for soil samples (Soils 1-5) collected at 0-20 cm depth S - adsorbed (mmol/kg); C_e - equilibrium concentration (mmol/dm³).

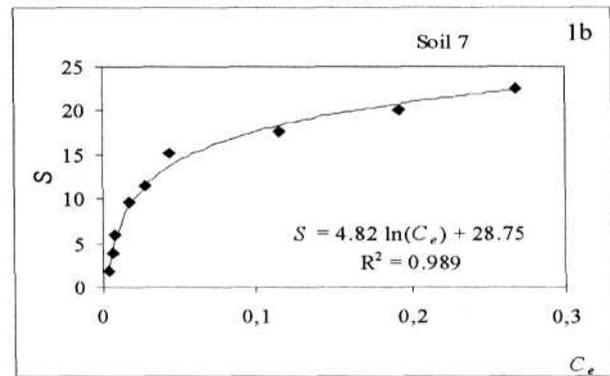
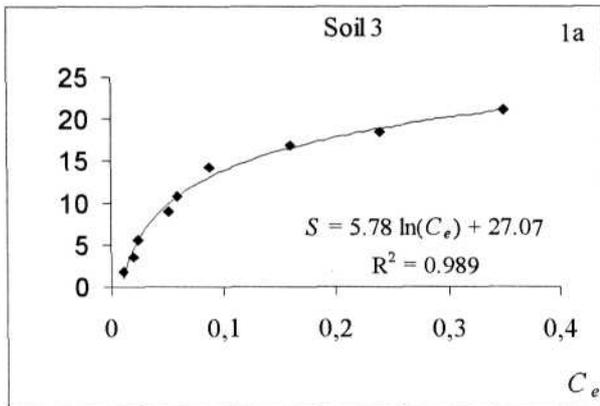
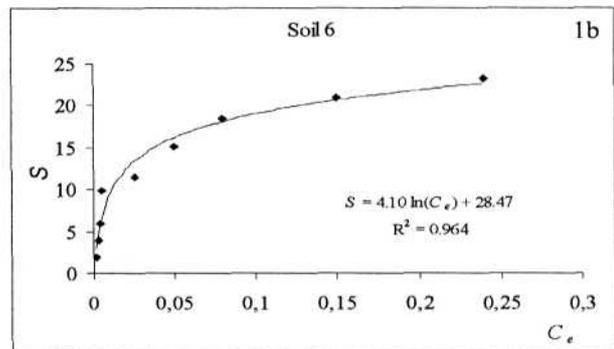
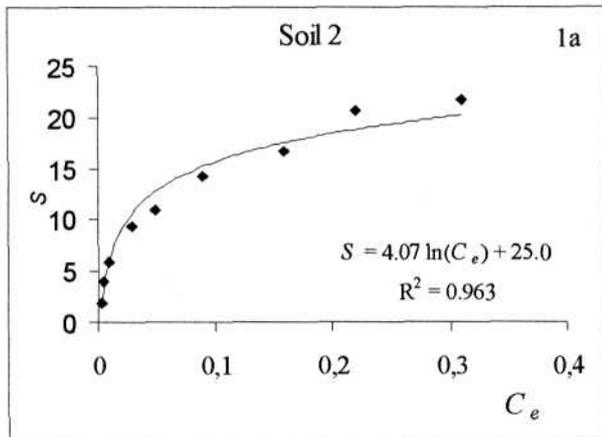
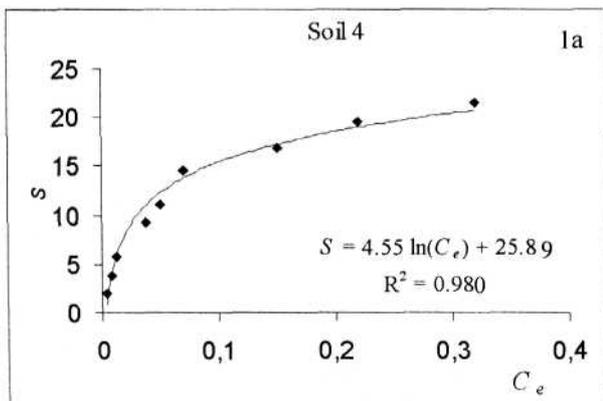


Fig. 1b. Representative Pb adsorption isotherms for soil samples (Soils 6, 7) collected at 20-40 cm depth. (Adnotations, see Fig. 1a).



Pb-saturated up to 90%, whereas the remaining ones were characterized by a higher saturation level (above 93%). This was clearly informative since the curves were not noticeably differentiated as well and the amount of "total Pb" strictly delimitates both groups of soil samples. The search for any causes of this discrepancy was not solved by the following linear regression equations, ($P < 0.05$):

$$K_F = -0.03 \text{ Pb}_{\text{Tot}} + 46.9; \quad (r = -0.37); \quad R^2 = 14\% \quad (7)$$

and

$$\text{Pb}_{\text{Tot}} = 0.094 \text{ Fe} - 13.6; \quad (r = 0.50); \quad R^2 = 26\% \quad (8)$$

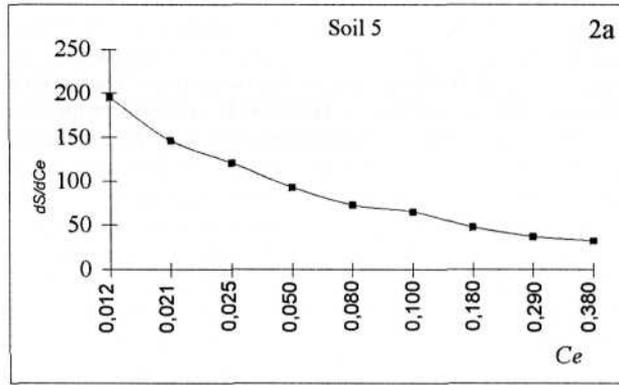
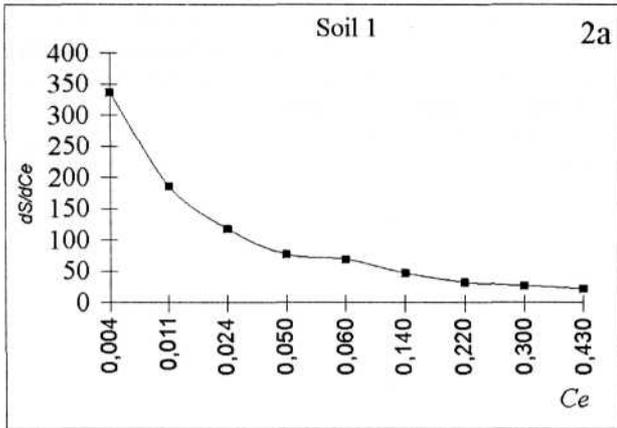


Fig. 2a. Variation of the buffering index (dS/dC_e) with the equilibrium Pb concentration (C_e) for soil samples (Soils 1-5) at the depth: 0-20 cm.

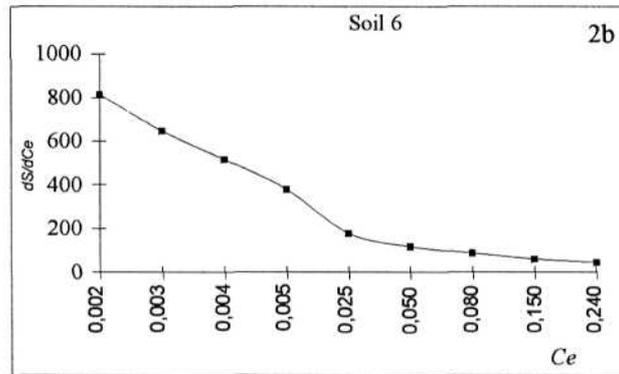
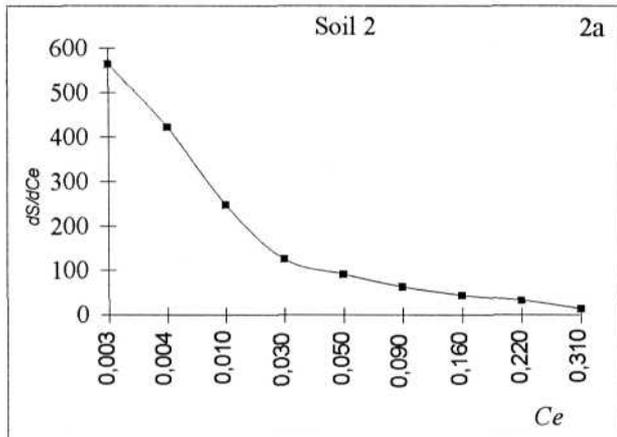
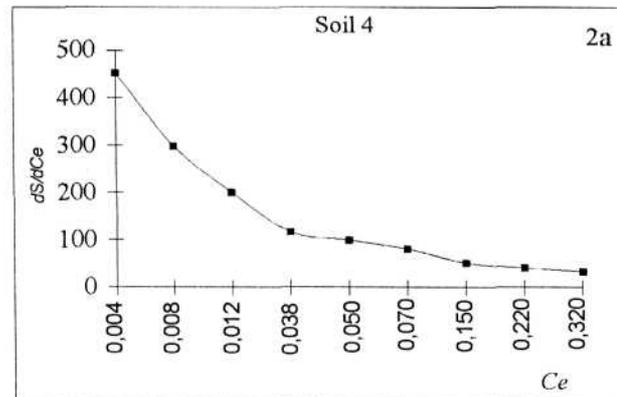
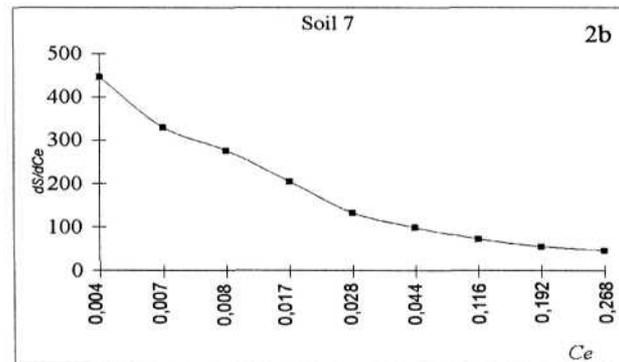
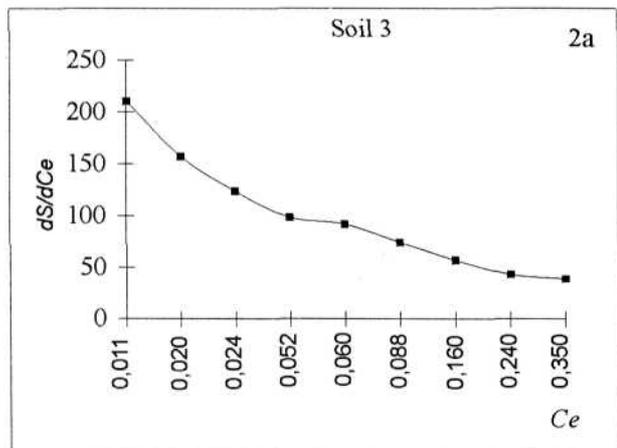


Fig. 2b. Variation of the buffering index (dS/dC_e) with the equilibrium concentration (C_e) for soils (Soils 6,7) at the depth: 20-40 cm.



The above-reported analysis partly revealed the possibility of misinterpretation based only on K_F and n parameters. Buchter et al. [4] have reported significant relationships between these two Freundlich parameters and soil properties and focussed on the predominant role of pH. In our work K_F also showed a strong relationship with pH, and moderately with clay, CEC and organic carbon (equ. 5 and 6). This stressing impact of soil pH on the retention of Pb could be expected since the tested soils were typically acidic.

Theoretically and experimentally the Freundlich equation assumes no maximal adsorption level with increasing the concentration of any element in the soil solution. Buffering index values showed that this assumption may be

partly verified mainly in sandy acidic soils and some maximal adsorption point could be expected as illustrated by Figures 1a and 1b (flattening of the isotherms). The lack of high correlation coefficients between K_F and soil properties as well as „total Pb” and the latter ones may be attributed first to the specificity of acidic agroforest soils and additionally to their presumable anthropogenic origin.

The estimation of a potential adsorption/desorption process poses serious difficulties and generally requires the solution of several equations. This complexity occurs strictly in organic (or organo-mineral) soils as well as some synthetic adsorbents presenting multilayers adsorption sites [7, 21]. Soil samples analyzed in the current work are mostly sandy and probably exhibit a monolayer adsorption site. In this order adsorption results may fit to the Langmuir one-surface equation. This is a matter of a further comparative study.

Appendix

(for equations 1, 2, 3)

dS/dC_e - buffering index,

S - amount of Pb retained by the soil, (mmol/kg),

S_0 - amount of Pb already present in the soil, (mmol/kg),

K_F - Freundlich sorption parameter, (dm^3/kg),

n - (dimensionless).

(for equation 4)

C_i - initial concentration of Pb in the solution, (mmol/ dm^3),

C_e - equilibrium Pb concentration, (mmol/ dm^3),

V - volume of the solution (dm^3),

W - weight of soil sample (kg).

Conclusions

1. Soil pH had a greater influence on K_F values whereas clay and organic matter content exerted a moderate role.
2. Free iron and manganese oxides did not reveal any close relationship with K_F and total Pb content.
3. Estimation of Pb sorption on the basis of buffering indices gave more practical approaches than made by the retention parameters K_F and n .
4. Potential Pb phytocontamination may take place with regard to the relatively poor sorptive complex of all soils.

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