

The Impact of Additional Pb Input on the Dynamics of Pb-Enriched Agricultural Soils

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Abstract

Agricultural ecosystems are differently sensitive to heavy metal inputs, which at present are directly related to human activities. Lead is of particular concern due to its ability to threaten soil quality and human health. The investigated soil samples were collected from different agricultural soils (under cereal croppings) moderately subjected to activity of the Głogów Copper Smelter (Poland). They consisted of an acidic soil (Dystric Gleyic Fluvisols – S_1) and three near neutral to slightly alkaline soils (Haplic Luvisols – S_2 , Gleyic Fluvisols – S_3 and Mollic Gleyic Fluvisols – S_4). These soils were tested in order to determine the impact of additional Pb inputs on its dynamics and mobility. Of all the soils studied, S_2 , S_3 and S_4 have exhibited higher acid buffer capacities than S_1 . Lead sorption parameters, such as Langmuir adsorption maximum (a_{max}) and parameters related to interaction energies (b) as well as the Freundlich partition parameter (K_F), were used for comparing the reactivity and dynamics of added Pb into these soils. The data showed that S_2 , S_3 and S_4 retained more Pb than did S_1 , characterized by low specific surface area (SSA) and cation exchange capacity (CEC). Charge-based (SD_{CEC}) and specific surface-based (SD_{SSA}) sorption densities were also used for evaluating the direct impact of additional Pb inputs. These parameters revealed that S_2 , S_3 and S_4 may support greater inputs of Pb with less threat to its mobility, in contrast to S_1 . Therefore, any practices leading to additional Pb inputs into the latter soil may result in serious Pb mobility. The negative values of the Gibbs free energy changes (ΔG°) for Pb dynamics in the studied soils confirm that the ion exchange process proceeded naturally and spontaneously with a markedly high affinity for Pb ions developed by S_2 , S_3 and S_4 , and low affinity by S_1 .

Keywords: lead dynamics, isotherms, charge densities, Gibbs free energy

Introduction

Lead contamination of soils is of great environmental concern and has been the subject of increasing attention [1-4]. It is one of the most widespread elemental contaminants worldwide [5] and is reported to cause anemia, kidney diseases, brain damage, high blood pressure, abnormal vitamin D metabolism and, in some cases, death [6]. The release of this metal via increasing exploitation and transformation of the earth's raw materials (fossil fu-

els and minerals, basically) have resulted in buildup of wastes (industrial, urban and agricultural) in which Pb concentration may reach several thousand milligrams per kilogram [7, 8, 9].

Soils are an important sink for Pb due to their high metal retention capacities. In many cases, much of the Pb in uncontaminated and contaminated soil is not present in readily available fractions, which may vary from <1 to 10% [10, 11]. Therefore, the persistence and mobility of Pb in these soils should be dictated by the extent to which Pb is sorbed to solid phases, which is a function of reactions affecting surface charge and ion density [12, 13, 14].

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

Soil type (N ₀)	Particle size (mm)			pH	Organic carbon (g kg ⁻¹)	SSA ^b (m ² g ⁻¹)	CEC (cmol ₍₊₎ kg ⁻¹)	CaCO ₃ (%)	EA ^d , (cmol ₍₊₎ kg ⁻¹)
	1.0-0.05	0.05-0.002	< 0.002						
	%								
^a S ₁	79	18	3	5.00	5.61	9.44	5.97	- ^c	2.43
S ₂	56	36	8	6.86	14.94	25.17	13.18	-	0.93
S ₃	75	21	4	7.60	12.05	37.41	15.50	2.15	-
S ₄	42	42	16	6.95	18.28	72.03	21.29	-	0.90

^a: S₁, S₂, S₃, and S₄ for Dystric-Gleyic Fluvisols, Haplic Luvisols, Gleyic Fluvisols and Molli-Gleyic Fluvisols, respectively. ^b: Specific surface area; ^c: not detected; ^d: Exchangeable Acidity.

Lead sorption and release in soils generally involve a wide range of reactions such as precipitation-dissolution and ion exchange processes [15, 16]. Several mathematical approaches have been used for describing the behavior/affinity of heavy metals (Pb among others) at the interface of soil colloid and water molecules [17, 18]. Of these models, Langmuir and Freundlich adsorption isotherms are two of the most frequently used [19]. The classical Langmuir isotherm expresses the occurrence of a monomolecular ion layer [20]. Adsorption parameters obtained from this isotherm provide limited details since they do not describe mechanisms involved in metal sorption as pointed out by Harter and Baker [21], Sposito [22], Veith and Sposito [23]. However, the usefulness of Langmuir equations in summarizing a mass of adsorption maxima for several soils is reported in some works [24, 25]. The most important multi-site adsorption isotherm for heterogeneous surfaces is the Freundlich adsorption isotherm, which in turn is purely empirical [19, 26]. It implies that the energy of adsorption on a homogeneous surface is independent of surface coverage. One of the major disadvantages of the Freundlich equation is that it does not predict an adsorption maximum but only a sorption capacity parameter. Therefore, interpretation of any adsorption mechanisms solely on the basis of Freundlich parameters may be speculative [19].

Understanding the dynamics of additional Pb inputs into soils is particularly important as these reactions dictate the strength of the metal-soil surface interaction. On a relative basis, exchange reactions may render Pb most labile, whereas the inner sphere complex formation and coprecipitation with a soil's surface cause Pb to be retained strongly and in many cases nearly irreversibly [13]. Most adsorption processes are the result of surface charges and ion densities at the soil solid phase. This is characteristic for each soil and the evaluation of these parameters for agricultural soils will provide pertinent information on the potentiality of Pb release (mobility) in these soils.

The aim of this paper is to assess the impact of additional Pb inputs on its dynamics and mobility in selected agricultural soils. Lead reactivity/sorption was evaluated on the basis of Langmuir and Freundlich parameters cal-

culated from relevant isotherms. Specific attention was given to surface charges, sorption densities and energy changes in order to elucidate the direct impact of additional Pb inputs and any probable threat of its mobility.

Material and Methods

The soils investigated were sampled at a depth 0-20 cm from selected agricultural lands (under cereal croppings) moderately subjected to the activity of the Głogów Copper Smelter, GCS (N 51°41'03" and E 15°57'12", Poland). Soils were air-dried and crushed to pass a 1.0 mm screen. Granulometric composition was determined according to the aerometric method of Bouyoucos-Casagrande, [27] and soil classification was made according to World Reference Base (WRB) [28]. On the basis of the textural class, soil samples were classified as Dystric-Gleyic Fluvisols (S₁), Haplic Luvisols (S₂), Gleyic Fluvisols (S₃) and Molli-Gleyic Fluvisols (S₄), as listed in Table 1. Organic carbon was determined by the Walkley-Black method as reported by Nelson and Sommers [29] and soil pH (w/v, 1:5) potentiometrically measured in 0.010 mole CaCl₂ dm⁻³ suspension Polska Norma [30]. Soil samples were additionally analyzed for carbonate content by the Scheibler method. Cation exchange capacity (CEC) and exchangeable acidity (EA) were determined by the Mehlich method (at pH 8.2) modified by Kociałkowski and Ratajczak [31]. Buffer curves were drawn according to Arrhenius with Brenner and Kappen modification [32] by adding increasing amounts of 0.1 mol HCl dm⁻³ and 0.1 mol NaOH dm⁻³ to soil samples, which, after 24 hours, was followed by potentiometric pH measurements. The specific surface area was estimated by EGME (Ethylene Glycol Monoethyl Ether) as suggested by Carter et al. [33]. Total lead content was determined in extracts obtained by digesting 1.00 g of soil in 15 cm³ of *Aqua regia* (concentrated HCl:HNO₃, ratio 3:1) for 2 hours and at 100°C, whereas exchangeable and organically bound Pb forms were extracted by DTPA (diethylenetriaminepentaacetic acid) according to Lindsay and Norvell [34]. All extractions were run in duplication. Lead was determined

by the FAAS method (Flame Atomic Absorption Spectrophotometry, Varian 250 plus).

Batch Equilibrium Studies

Lead concentrations for sorption/dynamics studies were prepared from $\text{Pb}(\text{NO}_3)_2$ reagents by dissolving appropriate amounts into $0.010 \text{ mole Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O dm}^{-3}$ solution (used as background electrolyte). The finally targeted Pb concentrations were 0.2, 0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8, and 2.0 mmol dm^{-3} and designated as initial Pb concentrations (C_i). The use of $0.010 \text{ mole Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O dm}^{-3}$ was an attempt to approximate the electrolyte environment of soils in the field [3]. Nitrate was chosen because of its poor ability to complex metallic cations [35]. Due to the great heterogeneity of soil samples under study, some preliminary tests were carried out in order to find out an optimal soil-to-solution ratio and proper reaction time to reach maximal equilibrium stage. It was found, on average, that from 53% (for S_1) to more than 94% (for S_2 , S_3 and S_4) of Pb initially added was sorbed after 16 hours of contact time. Based on these tests, lead solutions were added at soil-to-solution ratios of 1:15; 0.30:15; 0.20:15 and 0.15:15 for soils S_1 , S_2 , S_3 and S_4 , respectively, in 2 replicates in a series of polyethylene centrifuge tubes and shaken on a rotative shaker for two hours, after which mixtures were allowed to equilibrate for 24 hours and filtered. The pH of equilibrium solutions was measured. The adsorbed amounts of Pb were calculated as the difference between Pb initially added (C_i) and that remaining in solution after reaction with soils (i.e. C_e), accordingly:

$$S_{pb} = (C_i - C_e) V / W + CV \quad (1)$$

(See appendix for description)

The CV (correction value = amount of Pb previously retained by soils) value is frequently omitted, otherwise not specified [18, 36, 37, 38]. This assumes that the metal(s) was not previously present in the soil, far from the evidence referring to soil materials used for adsorption studies. The inclusion of the CV value [39, 40] is intended to level the amount of adsorbed Pb (S_{pb}) due to the fact that interaction occurs between CV and S_{pb} .

The linear Langmuir one-site isotherm as reported by Sposito [22] may be expressed as follows:

$$\frac{C_e}{S_{pb}} = \frac{1}{a_{\max} b} + \frac{C_e}{a_{\max}} \quad (2)$$

The Freundlich isotherm as an empirical equation (15), whose linear form is expressed as follows:

$$\log S_{pb} = \log K_F + n \log C_e \quad (3)$$

Sorption processes predominantly occur at surfaces of organic and inorganic colloids. Therefore, the expression

of these processes in terms of charge densities and "concentration" of substances (for examples ions) per unit area may be more meaningful. Non-specific adsorption through ion exchange is influenced by the surface charge, of which CEC is a measure. Then the density of charges (SD_{CEC}) potentially involved in Pb sorption was equated as follows:

$$SD_{CEC} = \frac{S_{pb} N_A}{CEC} \quad (4)$$

Lead sorption densities at any point were calculated as suggested by Schulte and Beese [41] and Zehetner and Wenzel [42]:

$$SD_{SSA} = \frac{S_{pb} N_A}{SSA} \quad (5)$$

The Pb ion exchange/adsorption isotherms were additionally used to evaluate thermodynamic changes of Pb dynamics in soils. Gibbs free energy was calculated on the basis of equilibrium constant as earlier suggested by Rawat *et al.* [17] and recently by Critter and Airoldi [43], by using the relationship:

$$\Delta G = -RT \ln K_R \quad (6)$$

where,

$$K_R = \frac{S_{pb}}{C_e} \quad (7)$$

Adsorption parameters were computed by using Sorption Software [44] and an Excel Spreadsheet.

Results and Discussion

Physical and chemical properties of soils are summarized in Table 1. The pH varied widely from the acidic (pH 5.00) soil (S_1) to slightly alkaline (pH 7.60) for soils S_2 , S_3 , S_4 . Organic carbon (C_{org}) content was relatively high (above 12.0 g kg^{-1}) except for S_1 with C_{org} amounting for 5.61 g kg^{-1} and a markedly low cation exchange capacity (CEC) of $5.97 \text{ cmol}_c \text{ kg}^{-1}$. On the other hand, soils S_2 , S_3 , and S_4 were characterized by CEC values 2.5 to 3.5 times higher than that reported for S_1 . The specific surface area (SSA) varied significantly from 9.44 to $72.03 \text{ m}^2 \text{ g}^{-1}$ and followed closely the same trend observed for CEC values. As shown in Table 2, total Pb content (Table 2) ranged between 18.7 and 184.4 mg kg^{-1} . The potentially available Pb fraction, expressed in terms of DTPA_{pb} , did not exceed 30% of the total Pb content even for the S_1 characterized by acidic medium and notably low level of C_{org} and CEC. Therefore, the relatively low level of DTPA_{pb} may be attributed to a strengthened Pb retention (soils buffering capacities) reducing Pb bioavailability. The outlook of soil buffering capacities expressed by buffer curves is illustrated in Fig. 1. The curves of all soils are similar in shape mainly for the alkaline buffer capacity but differed notably in their deviation from the standard curve in the case of the acid buffer capacity. Similar curve slopes were reported by Raczuk [45] for black earth and mucky soils. In the current work, in-

Table 2. Amounts of Pb extracted by *Aqua regia* (Pb_{Tot}) and by DTPA (Pb_{pb}) ($mg\ kg^{-1}$).

Soil type (N_o)	Pb_{Tot}	$DTPA_{pb}$	Pb (%) ^b
^a S_1	184.4	52.8	28.6
S_2	127.4	27.9	21.9
S_3	18.7	2.1	11.2
S_4	81.8	9.3	11.4

^a: S_1 , S_2 , S_3 , and S_4 for Dystric-Gleyic Fluvisols, Haplic Luvisols, Gleyic Fluvisols and Molli-Gleyic Fluvisols, respectively.

^b: Percentage of $DTPA_{pb}$ in Pb_{Tot}

investigated soils showed relatively less resistance to alkalization, since the addition of alkali (NaOH) caused pH changes which varied between 8.5 and 14.0. On the other hand, considerable changes in the curve slopes were recorded after the addition of only $3\ cm^3$ of $0.1\ mol\ HCl\ dm^{-3}$ to S_1 , causing a 6-unit pH decrease (from pH 8 to 2). Soils S_2 and S_4 exhibited notable resistance to acid impact as a result of high C_{org} and CEC, whereas a greater amount of acid (up to $15\ cm^3$) caused a slight pH change up to 2.5 pH unit for S_3 . The reactions occurring in this soil could be predominantly dictated by the presence of carbonates acting as a special "sink" for acid protons. At $25\ cm^3$ of acid addition to S_2 , S_3 , and S_4 , their pH values were stabilized near 2.0-3.0 at which point the soil reaction is thought to be affected by acid aluminium ion or acid organic matter extraction. Such observations were also reported by Clayton *et al.* [46] and Sparks [19], who examined the course of two buffer curve sections in the so-called pH jump and slow change.

Lead Dynamics and Sorption by Soils

Langmuir Parameters

Sorption isotherms were constructed to compare Pb dynamics between investigated soils as shown in Fig. 2. The

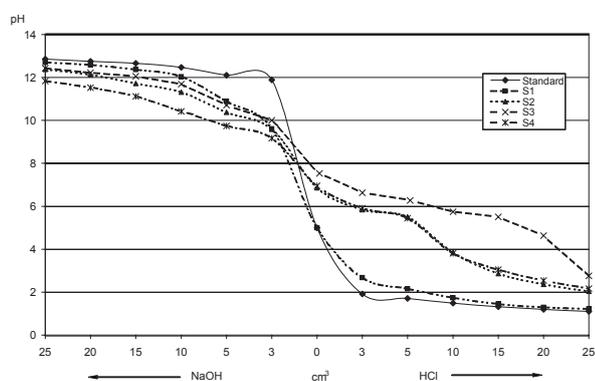
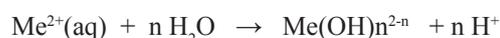


Fig. 1. Effect of base (NaOH) and acid (HCl) additions on changes in buffering capacities of agricultural soils.

formation of the first Pb molecule layer and consecutive ones obey the typical coulombic attraction strength: the closer the colloid surface the stronger the attraction between the negatively charged colloid surface and Pb ions. Amounts of adsorbed, S_{pb} , varied widely and amounted on average 11.4, 53.4, 80.2 and $101.1\ mmol_c\ kg^{-1}$ for the S_1 (imbedded in Fig. 2), S_2 , S_3 and S_4 , respectively [3]. At initial Pb concentration $C_i = 2.0\ mmol_c\ dm^{-3}$, the S_{pb} values followed the sequence $S_4 > S_3 > S_2 > S_1$, which was consistent with that observed for CEC, specific surface area (SSA), but was not in conformity with C_{org} , pH and clay content.

Lead is reported to exhibit a high affinity for most soil functional groups [47] as a result of small hydrated radius ($0.401\ nm$), which in turn creates suitable conditions for electrostatic and inner-sphere surface complexation reactions [13, 19]. Processes involved in Pb sorption should be of two basic types: specific and nonspecific exchange reactions, particularly for S_1 , S_2 and S_4 characterized by pH below 7.0 and chemisorption (precipitation) and/or exchange reactions in the case of S_3 (occurrence of appreciable levels of organic carbon and carbonate) with pH of 7.60. It was demonstrated by Schulthess and Huang [48] that the first degree of hydrolysis of Pb^{2+} ions ($Pb^{2+} \rightarrow PbOH^+$) occurs at $pH = 5.90$. According to Abd-Elfattah and Wada [49] and Elliot *et al.* [50], in neutral to alkaline soil conditions, the amounts of hydrated metals at the first degree of hydrolysis increase, which simultaneously enhances metal adsorption. The following reaction is generally suggested:



The soil solution pHs at the highest Pb inputs (Table 3) ranged between 6.15 and 6.95. Therefore, it can be expected that most Pb^{2+} ions may potentially undergo hydrolysis process to generate $PbOH^+$ ions preferentially adsorbed over Pb^{2+} ones as pointed out by some researchers [51, 52, 53]. The low solution pH (i.e., 4.80) recorded for the S_1 and the lowest amount of Pb being adsorbed could be attributed to the prevalence of Pb^{2+} ions, which in turn supports the postulate of Schulthess and Huang [48].

Most of the soils studied exhibited isotherm types belonging to the *H* and *L*-type [54]. The *H*-type (high affinity) isotherms observed for S_2 , S_3 and S_4 predominated for

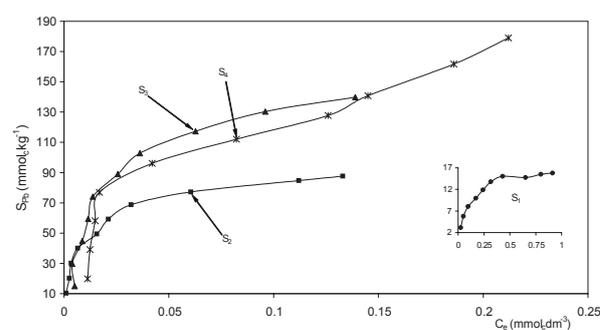


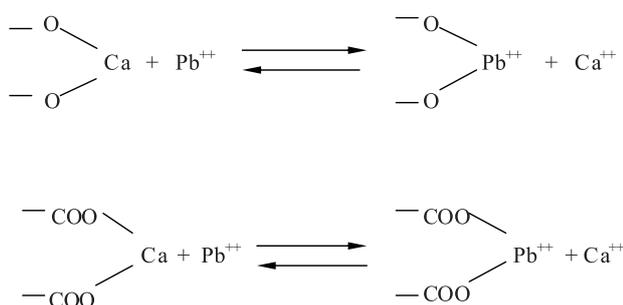
Fig. 2. Isotherms established between adsorbed Pb (SPb) and equilibrium concentration of Pb (C_e) in agricultural soils.

Table 3. Amounts of adsorbed Pb (S_{pb}) and Langmuir and Freundlich adsorption parameters of the soils.

Soil type (N_o)	S_{pb}	Equilibrium solution pH ^c	Langmuir parameters				Freundlich parameters		
			a_{max}	b	MBC	R^2	K_F	n	R^2
^a S ₁	11.4±4.5 ^b	4.80	17.7±0.8	8.9±0.4	157.5±6.8	0.997	19.3±2.9	0.463±0.09	0.907
S ₂	53.4±28.1	6.45	96.2±16.0	94.5±15.1	9090.9±1569.4	0.993	247.6±55.1	0.412±0.05	0.904
S ₃	80.2±42.9	6.95	161.3±46.7	41.3±7.7	6661.7±1448.0	0.964	476.0±124.7	0.526±0.08	0.808
S ₄	101.1±52.8	6.15	212.8±64.9	16.2±4.3	3447.4±1017.9	0.911	427.3±120.8	0.543±0.08	0.817

^a: S₁, S₂, S₃, and S₄ for Dystric Gleysols, Haplic Luvisols, Gleyic Fluvisols and Molli-Gleyic Fluvisols, respectively; ^b: Standard deviation; ^c: pH of the equilibrium solution at the highest Pb inputs ($C_i = 2.0 \text{ mmol}_c \text{ dm}^{-3}$).

initial Pb concentration (C_i) ranges varying from 0.2 to 0.8 $\text{mmol}_c \text{ dm}^{-3}$, over which isotherm slopes decreased to change to L -type isotherm (Langmuir) with increasing Pb solution concentrations (Fig. 2). Such adsorption behaviour could be explained by the high affinity of the adsorbent for the adsorbate at low concentrations, which then decreases as concentration increases. This trend was not conformed to the L -type isotherm developed by S₄, which exhibited a second shift in Pb sorption over $C_i = 1.2 \text{ mmol}_c \text{ dm}^{-3}$. According to Davranche *et al.* [12], the surface charge of carbonates is accommodated mainly by protonation/deprotonation reactions and, moreover, carbonates tend to control and set their charges. Soil S₃ contrarily to other soils contains carbonates, which strengthened Pb sorption reaching 80% of CEC at $C_i = 2.0 \text{ mmol}_c \text{ dm}^{-3}$ if compared to 62% (S₂), 72% (S₄) and 27% (S₁). Since the amount of Pb adsorbed did not exceed CEC, it could be because exchange reactions predominated. Therefore, the resulting isotherms (for S₃ and S₄, basically) should be attributed to an emergence of “new” sorptive sites due to ionization of surface OH and COOH groups as suggested by Abd-Elfattah and Wada [49]:



Such specific metal complex formation with deprotonated surface OH groups as bidentate and monodentate ligands has been earlier pointed out by Davis and Leckie [55] and Schindler *et al.*, [56] for various metal reactions on silica and other oxides.

The maximal buffering capacity (MBC , Table 3) exhibited by soils as a result of Pb sorption expresses the highest potential of soils to adsorb (a_{max}) and simultaneously tightly retain (b) Pb ions in the soil solid phase. The higher the MBC value, the stronger and more intense was

Pb sorption. On the basis of this parameter, soils may be ranked as follows: S₂ ($9090.9 \text{ dm}^3 \text{ kg}^{-1}$) > S₃ ($6661.7 \text{ dm}^3 \text{ kg}^{-1}$) > S₄ ($3447.4 \text{ dm}^3 \text{ kg}^{-1}$) > S₁ ($157.5 \text{ dm}^3 \text{ kg}^{-1}$). The sequence is not consistent with the adsorption maximum - a_{max} , but agrees with parameters related to energy of adsorption - b and to some extent with buffer curve shapes in the acid zone (Fig. 1). These results show that more complex processes were involved in Pb sorption.

Freundlich Parameters

One of the major disadvantages of the Freundlich equation is that it does not predict any adsorption maximum. The Freundlich partition parameter (K_F) implies that the energy of adsorption on a homogeneous surface is independent of the degree of saturation, and that adsorption process runs linearly. This postulate does not seem to be applicable to soils characterized by heterogeneous adsorption surfaces. Simple isotherms established by plotting amounts of adsorbed Pb (S_{pb}) versus its equilibrium concentration (C_e) (Fig. 2) did not support this assumption (emergence of plateau-type isotherms). Data reported in Table 3 clearly show differences in soil capacity to adsorb Pb ions, and the intensity of this process expressed by the constant n (slope intensity). This positive-valued empirical constant is widely reported to lie between 0 and 1 [42, 57, 58, 59], and significant isotherm curvature should be observed with n tending to 0, in opposite to linearity at n tending to 1. Mean values of n varied within a relatively narrow range (0.412-0.543), which means isotherm shapes were less steep (occurrence of curvature) and that most high energetic sorptive sites were occupied by Pb ions, with the remaining sorptive sites being characterized by low adsorption energies with increasing surface coverage. A similar observation was made by Narwal and Singh [60], who reported very steep curves at low Pb, Zn, Cu and Cd concentrations with the slopes becoming less steep when the concentration of metals in equilibrium solution increased. If we consider K_F parameters as expressing the whole soil capacity for Pb^{2+} adsorption, we observe that these values are strikingly low compared to Langmuir MBC . As shown in Equ. (3) the slope of this equation is expressed by $1/C_e^n$, which means for dilute equilibrium concentrations (i.e. $C_e \ll 1$), typically for strengthened Pb partition to soils solid

phase (i.e. S_2 , S_3 and S_4), K_F values will tend to increase in opposite to less dilute solutions as a result of weak Pb partitions as in the case of S_1 . Therefore, the low clay and organic matter contents promoting a low specific surface area (S_1) could have acted as limiting factors, which is in agreement with the findings of Buchter *et al.* [15] and Salim *et al.* [18].

Lead Charge-Based and Sorption Density Parameters

The distribution of sorptive sites on soil colloids is not uniform [19, 61]. For adsorption, cations are held either through electrostatic attraction (giving rise to ion exchange with surrounding ions) or by specific adsorption through surface complexation on organic and mineral substrates [62]. The affinity of soil colloids for lead ions, expressed in terms of ions per unit area (Fig. 3), interestingly showed the magnitude of the adsorption process. These plots clearly show that Pb adsorption did not proceed linearly. The first Pb adsorption step (up to curve inflections) may be due to the high energy sites, whereas the following one should be attributed to the emergence of sites characterized by relatively low energy. A general analysis of plots revealed that the lower the surface-based sorption density ($\log SD_{SSA}$) and equilibrium Pb concentrations ($\log C_e$), the higher the potential reactive sites for Pb ions and vice versa, as additionally reported in Table 4. Assuming that Pb potential adsorption took place throughout the whole specific surface area, then the potential sorption densities (mean values of $\log SD_{SSA} \times SSA$) of soils should amount to 7.69, 25.87, 38.53 and 61.29 $\times 10^{17}$ ions for the respective specific surface areas of S_1 , S_2 , S_3 and S_4 . If the potential sorption density of the S_1 should be considered as reference ($S_1 = 7.69 \times 10^{17}$ ions m^{-2}), then we can estimate that an approximate 3, 5 and 8-fold increase in solution concentration following Pb inputs, for soils S_2 , S_3 and S_4 , respectively, is not to be expected. Practically, the S_1 , characterized by low potential sorption density values, has very limited capacity for Pb sorption and any excess Pb inputs should lead to its mobility and hence any environmental concern.

Since cation exchange capacity may be considered as the whole soil reactive system, it may be informative also to express Pb reaction with soil colloids in terms of num-

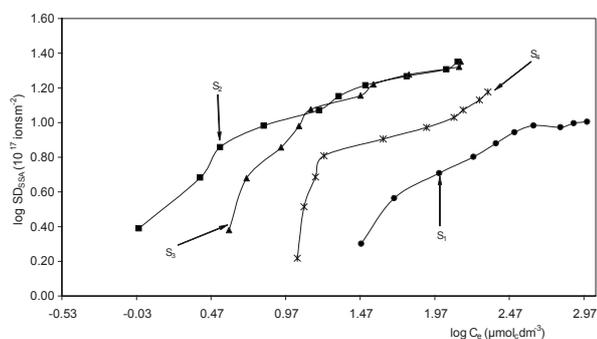


Fig. 3. Relationship between specific surface-based Pb sorption density (SD_{SSA}) and equilibrium concentration of Pb (C_e) in agricultural soils.

Table 4. Lead specific surface area sorption density (SD_{SSA}) and charge-based (SD_{CEC}) parameters.

Soil type (N_0)	$\log SD_{SSA} \times 10^{17}$		$\log SD_{CEC} \times 10^{17}$	
	Range	Mean \pm SD ^b	Range	Mean \pm SD
^a S_1	0.3011.004	0.815 \pm 0.231	6.29-7.26	6.93 \pm 0.304
S_2	0.3891.350	1.028 \pm 0.307	5.67-6.63	6.30 \pm 0.308
S_3	0.3801.352	1.030 \pm 0.313	5.76-6.74	6.41 \pm 0.313
S_4	0.2171.176	0.851 \pm 0.303	5.75-6.70	6.38 \pm 0.303

^a: S_1 , S_2 , S_3 , and S_4 for Dystri-Gleyic Fluvisols, Haplic Luvisols, Gleyic Fluvisols and Molli-Gleyic Fluvisols, respectively;
^b: Standard deviation

ber of Pb ions per moles of charges developed within the CEC (Fig. 4, Table 4). The $\log SD_{CEC}$ values at inflections amounted to 6.59, 6.14, 6.46 and 6.34 $\times 10^{17}$ ions mol^{-1} , for S_1 , S_2 , S_3 and S_4 , respectively. This process seemed to be very intensive, since about 90, 92, 96, and 95% of all moles of charges occupied by Pb ions were potentially neutralized just at the emergence of low-energy sites (beyond inflections) for S_1 , S_2 , S_3 and S_4 , respectively. According to Boehringer [63] and Bunzl *et al.* [64], organic matter may frequently exhibit a large pool of high-energy sites, thus creating conditions of an apparent specific adsorption, especially for Pb. The latter belongs to the group of metals (i.e. Zn and Pb) that tend to be specifically adsorbed [49]. On the other hand, the precipitation reactions, typically recognized for carbonates as a “chemical sink,” may contribute to the formation of additional “sorptive” sites (S_3 , for instance). The joint effect of these physically and chemically distinct systems (organic matter and carbonates) was believed to promote such Pb adsorption.

Lead Adsorption and Free Energy Changes

The values of K_R and b as listed in Table 5 indicate the highest stability for the formation of Pb – soil complexes

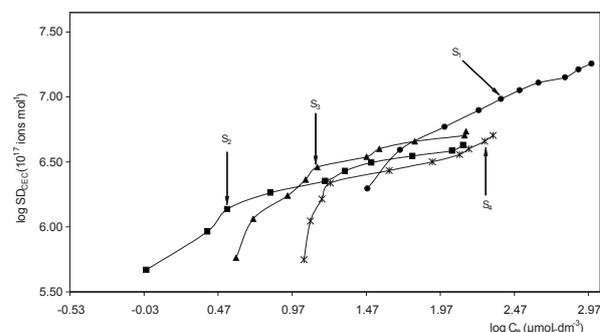


Fig. 4. Relationship between charge-based Pb sorption density (SD_{CEC}) and equilibrium concentration of Pb (C_e) in agricultural soils.

Table 5. Gibbs free energy changes (ΔG°) based on Rawat (K_R) and Langmuir (b) constants for Pb adsorption at 293 K.

Soil type (N_o)	$K_R \times 10^2$	ΔG°	$b \times 10^2$	ΔG°
$^a S_1$	0.54 ± 0.4^b	-9.39 ± 1.7	0.12 ± 0.12	-6.67 ± 1.3
S_2	47.85 ± 39.7	-19.94 ± 2.6	1.49 ± 1.31	-12.89 ± 1.6
S_3	35.88 ± 21.6	-19.78 ± 1.8	1.17 ± 1.09	-12.26 ± 1.8
S_4	20.73 ± 13.6	-18.45 ± 1.6	0.38 ± 0.34	-9.43 ± 1.7

*: $S_1, S_2, S_3,$ and S_4 for Dystri-Gleyic Fluvisols, Haplic Luvisols, Gleyic Fluvisols and Molli-Gleyic Fluvisols, respectively;
^b: Standard deviation

and may predict the mobility or even bioavailability of Pb in the soil [43]. The amount of adsorbed Pb (S_{pb}) increased simultaneously with increasing soil cation exchange capacities (CEC) and specific surface area (SSA), which is not in line with the reverse sequence exhibited by K_R and b , except for S_1 . The involved process results in fact that soils with large SSA and CEC developed a high-affinity-type reaction with Pb as shown in Fig. 5 (free energy based- K_R constant versus Pb adsorbed). It is important to point out that agricultural soils (i.e. S_2, S_3 and S_4) have decidedly developed higher affinity and properly greatest energy (ΔG°), which tend to decrease with increasing Pb adsorption. This process was more pronounced in the case of the S_1 characterized by low Pb adsorption and energy (mean value $-9.39 \text{ kJ mol}^{-1}$). The negative values of the Gibbs free energy changes (ΔG°) for the adsorption of Pb by soils confirms that the ion exchange – sorption process has a natural tendency to proceed spontaneously with a high affinity toward Pb ions.

Conclusions

Investigated agricultural soils consisted of an acidic (Dystri-Gleyic Fluvisols – S_1) and near neutral to slightly

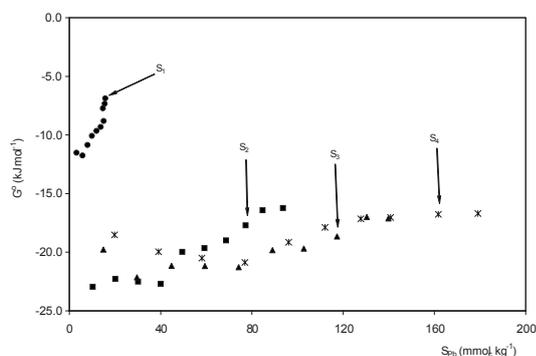


Fig. 5. Relationship between Gibbs free energy of changes (ΔG°) and amounts of Pb adsorbed (S_{pb}) by agricultural soils.

alkaline soils (Haplic Luvisols – S_2 , Gleyic Fluvisols – S_3 and Molli-Gleyic Fluvisols – S_4). Buffer curves indicate that S_2, S_3 and S_4 have exhibited higher acid buffer capacities than S_1 . Adsorption parameters calculated by using Langmuir and Freundlich isotherms reveal that S_2, S_3 and S_4 adsorbed decidedly more Pb than did S_1 . The percentage share of Pb adsorbed within the CEC was evaluated to 80% for S_3 , 72% for S_4 , 62% for S_2 and only 27% for S_1 . The use of charge-based and specific surface-based sorption densities for evaluating the capacities of soils for Pb adsorption showed clearly that S_2, S_3 and S_4 may support greater inputs of Pb ions with less threat of Pb mobility and bioavailability, compared to S_1 . Any practices leading to additional Pb inputs into the latter soil should be avoided due to its low specific surface area and cation exchange capacity. The negative values of the Gibbs free energy changes (ΔG°) for Pb adsorption by soils confirm that ion exchange – sorption process proceeded naturally and spontaneously with a markedly high affinity for Pb ions developed by S_2, S_3 and S_4 and low affinity by S_1 . Lead mobility and possible transfer to plants basically should not be of great concern for S_2, S_3 and S_4 .

Appendix

- C_i - initial Pb concentration in solution before reaction ($\text{mmol}_c \text{ dm}^{-3}$)
- C_e - equilibrium Pb concentration in the soil extracts ($\text{mmol}_c \text{ dm}^{-3}$)
- CV - correction value (amount of Pb extracted by DTPA) ($\text{mmol}_c \text{ kg}^{-1}$)
- S_{pb} - amount of adsorbed Pb ($\text{mmol}_c \text{ kg}^{-1}$)
- a_{max} - adsorption maxima ($\text{mmol}_c \text{ kg}^{-1}$)
- b - bonding term relative to interaction energies ($\text{dm}^3 \text{ mmol}_c^{-1}$)
- V - volume of the initial solution (dm^3)
- W - weight of soil sample (kg)
- K_F - Freundlich partition parameter ($\text{mmol}_c^{1-n} \cdot (\text{dm}^3)^n \text{ kg}^{-1}$)
- n - sorption constant (shape intensity, dimensionless) expresses the slope of the adsorption isotherm
- MBC - maximal buffering capacity ($\text{dm}^3 \text{ kg}^{-1}$)
- SD_{CEC} - charge-based sorption density (ions mol_c^{-1})
- SD_{SSA} - Sorption density based on the specific surface area (ions m^{-2})
- ΔG° - Gibbs free energy (J mole^{-1})
- R - Universal gas constant ($8.314 \text{ J mole}^{-1} \text{ K}^{-1}$)
- T - Absolute temperature, (273 K)
- K_R - Rawat equilibrium constant ($\text{dm}^3 \text{ kg}^{-1}$)

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