

# Influence of Correction Values on Sorption Parameters: Case of Lead

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## Abstract

Three adsorption equations were applied to verify the influence of correction values (*CV*) on adsorption parameters calculated using Langmuir, Freundlich and Gunary isotherms. It was found that the inclusion or not of the correction values into the Langmuir equation did not yield appreciable differences either for  $a_{\max}$  or  $b$  parameters in the case of soils with relatively high organic matter content, cation exchange capacity and neutral pH. For the Freundlich equation, the higher the correction values the lower the partition parameters. Maximum adsorption parameters ( $a_{\max}$ ) calculated from the Gunary equation were proportionally related to correction values. The higher the correction values the higher the  $a_{\max}$  parameters. On the basis of the current results it seemed that the goodness-of-fit criteria for analytical data to adsorption equations herein applied may be partially related to correction values. Ideally, the sorption studies would be determined in systems in which the surface would be free of the adsorbate ion. Usually this restriction is far not feasible, mainly in soil environment.

**Keywords:** Lead, sorption, correction value, Langmuir one-site, Freundlich, Gunary isotherms.

## Introduction

The behavior of heavy metals in soil has gained greater attention during the last two decades due to the increasing disposal of metals into this environment from anthropogenic activities such as dumping of industrial effluents and agricultural applications of sewage sludge, fertilizers and pesticides [1, 2, 3, 4]. The subsequent fate of metals incorporated to soils is primarily governed by physical interactions and chemical reactions such as sorption and release between solute and soil body [5, 6]. Whatever the mechanism may be, sorption processes in soils predominantly determine the mobility, activity and bioavailability of metals which, in turn, may be undoubtedly influenced by the concentration of metals in the soil.

There are many reports available for evaluating sorption data by applying various mathematical models. If we

usually consider in sorption studies the direct or even indirect effect of soil properties (i.e. pH, organic carbon, clay, oxides) we must unavoidably also take into account the level of all soil elements (metal or nonmetal) under study. This was earlier pointed out by Olsen and Watanabe, [7] with the so-called correction for initial surface phosphate in phosphorus adsorption studies by using one-surface Langmuir isotherm. In the case of the Freundlich isotherm Nychas [8] and later Asimakopoulos [9] made appropriate allowances for soil phosphorus by designating it as  $q$ , i.e. as the amount of phosphorus already present in the soil. The extension of the Freundlich isotherm for assessing the curve by  $BC^D$  (where  $B$  - the commonly reported  $n$ ,  $C$  - equilibrium concentration and  $D$  - amount of P in the soil) was suggested by Sibbesen [10].

Another adsorption equation was elaborated by Gunary [11]. The data used to fit the model were ext-

ended by the so-called phosphate already adsorbed in the soil. The model assumed that the soil would adsorb only a given amount of phosphorus (relative to the Langmuir equation) and simultaneously the sorption process would go on indefinitely (relatively to the Freundlich equation) with a possibility to calculate a unique maximum adsorption parameter.

Studies on heavy metal sorption by soil materials carried out by using the above-mentioned or other isotherms did not generally take into account the content of metals already present in the soil. Ideally the adsorption would be determined in a system in which the surface were free of the adsorbate. This restriction is usually not feasible. A correction for the initial metal (soil metal) has to be made by adding the amount of metal determined by a separate analysis to that gained from the equilibrating solution. A similar approach was adopted by Diatta and Kociatkowski [12]; Kocialkowski et al. [13] on zinc and lead sorption by soils, respectively. The adsorption data obtained by including the correction value (amount of any element already in the soil) may be erroneously comparable with results in which this parameter is not included. So the risk of misinterpretation of sorption parameters in the second case has to be seriously considered.

The purpose of this paper was to verify whether or not:

- i) the inclusion of different correction values into the amount of lead adsorbed during equilibration affects sorption parameters, and
- ii) there are some relationships between the corrected and uncorrected sorption parameters and the particular soil properties.

## Materials and Methods

Soils were collected at two different sites (0-20 cm depth) within the Glogow Sanitary Zone (GSZ) (Poland), and from agricultural soils (AS) neighboring the sanitary zone, in order to ensure a heterogeneity of the soil samples. These soil samples were divided into two groups on the basis of total lead content in Aqua regia (*Ar*): AS, up to  $1.24 \text{ cmol}_c\text{kg}^{-1}$  (for soils Nr 1, 2, 3) and GSZ, above  $1.24 \text{ cmol}_c\text{kg}^{-1}$  (for soils Nr 4, 5, 6 and 7). All soils were air-dried and passed through a 1 mm mesh sieve before analysis. Soil particle size was determined by the Casagrande-Proszynski areometer method, organic carbon ( $C_{\text{org}}$ ) by Tiurin's method [14], and pH potentiometrically in 0.01 mol  $\text{CaCl}_2$  suspension according to Polska Norma [15]. The modified Mehlich method [16] was used for cation exchange capacity (CEC) determination. Lead was extracted in duplicate with the  $\text{HCl}:\text{HNO}_3$  (ratio 3:1 v/v) concentrated mixture namely Aqua regia [17]. This amount represented the total Pb. The second extractant used was 2 mol  $\text{HNO}_3$  [18] and the third was 0.005 mol DTPA (diethylenetriaminepentaacetic acid) developed by Lindsay and Norvell [19].

### Equilibration and Adsorption Studies

All soil samples were equilibrated with lead concentrations varying from 0.1 to  $2.0 \text{ mmol}_c\text{L}^{-1}$  as  $\text{Pb}(\text{NO}_3)_2$  in a 0.01 mol  $\text{Ca}(\text{NO}_3)_2$  solution (background electrolyte). Soil/solution ratio was kept constant at 1:10 (w/v) in a series of polyethylene centrifuge tubes with shaking

Table 1. Physical and chemical soil properties and amounts of Pb extracted by three different extractants.

Soil type <sup>a</sup> (number)	Soil particles ( $\text{g kg}^{-1}$ )		$C_{\text{org}}$ ( $\text{g kg}^{-1}$ )	CEC ( $\text{cmol}_c\text{kg}^{-1}$ )	pH $\text{CaCl}_2$	Pb extracted ( $\text{cmol}_c\text{kg}^{-1}$ )		
	0.1 – 0.02 (mm)	< 0.002 <sup>c</sup>				Aqua regia	2 mol $\text{HNO}_3$	DTPA <sub>(7,3)</sub>
Loam (1)	270.0	420.0	19.61	21.33	6.9	0.80	0.45	0.28
Loamy sand (2)	250.0	200.0	18.43	15.51	7.6	0.18	0.07	0.03
Sandy loam (3)	420.0	220.0	14.04	13.25	6.8	1.24	0.88	0.28
Loamy sand (4)	360.0	230.0	9.62	5.44	4.8	4.20	2.94	0.65
Sandy loam (5)	435.0	230.0	7.63	5.61	4.8	1.80	1.12	0.74
Sandy loam (6)	450.0	215.0	7.80	5.20	4.7	2.78	1.29	0.50
Sandy loam (7)	270.0	160.0	7.81	5.54	4.8	3.00	2.20	0.34
COV (%) <sup>b</sup>	25	35	43	63	–	70	78	61

<sup>a</sup> According to Soil Survey Division Staff (1993); For additional details refer to "Materials and methods"; <sup>b</sup> Coefficient of variation; <sup>c</sup> Clay (here and after).

time lasting two hours in a rotating shaker. The suspension was filtered after 24 hours of equilibration. Lead in the equilibrium solution as well as that in Aqua regia (*Ar*), 2 mol HNO<sub>3</sub> and DTPA were determined by the FAAS method (Flamme Atomic Absorption Spectrophotometry, Varian Spectra 250 plus). Adsorption data presented in the work were computed by using Sorption Softwares (IZOTERMY) especially elaborated for sorption studies. Amount of Pb in the soil solid phase ( $S$  = adsorbed) was calculated as the difference between the initial ( $C_o$ ) and equilibrium Pb concentration ( $C_e$ ). This amount was corrected by the inclusion or not of a correction value expressed as  $CV$ , the amount of Pb extracted by Aqua regia, HNO<sub>3</sub> and DTPA, (Table 1). Units of  $CV$  (cmol<sub>c</sub> kg<sup>-1</sup>) were converted into mmol<sub>c</sub>kg<sup>-1</sup> prior to use in equations listed below. Equilibration data are means of two replications and amounts of Pb retained by the soils were calculated as follows:

# with correction value (+ $CV$ )

$$S = (C_o - C_e) \frac{V}{W} + CV \quad (1a)$$

# without correction value

$$S = (C_o - C_e) \frac{V}{W} \quad (1b)$$

Equation 1b is rewritten to outline the basic difference in the expression of both equations 1a and 1b. Amounts of Pb adsorbed ( $S$ ) and the further adsorption parameters calculated on the basis of equation 1b are termed uncorrected (correction value not included).

Langmuir one-site, Freundlich and Gunary adsorption parameters were obtained from adsorption isotherms as follows:

a) Langmuir one-site adsorption isotherm

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

b) Freundlich adsorption isotherm

$$S = K_F C_e^n \quad (3)$$

c) and the equation developed by Gunary [11]

$$\frac{C_e}{S} = A + B C_e + D \sqrt{C_e} \quad (4)$$

$A$ ,  $B$ , and  $D$  are constants. Adsorption maximum ( $a_{\max}$ ) can be calculated under the following conditions:

$$\frac{1}{S} = B + \frac{A}{C_e} + \frac{D}{\sqrt{C_e}} \quad a_{\max} = \frac{1}{B}; \quad (= S, \text{ for } C_e \rightarrow \infty) \quad (5)$$

(See appendix for abbreviations)

Statistical analysis and correlation coefficients between soil physical and chemical properties and corn-

puted adsorption parameters were made using Statgraphics Software.

## Results and Discussion

The geochemistry of lead depends on numerous soil physical and chemical properties of soil and, as can be expected, also on Pb content in the soil. While there is an abundance of information dealing with lead sorption by soils [13, 20], virtually nothing is known about the influence of lead already present in the soil on the changes of sorption parameters. It is widely reported that equilibration processes in soils are reversible. If we disregard precipitation, the reversibility may greatly be related to the intensity of the formation of the particular adsorptive layers on organic as well as clay surfaces. The latter ones can be presumably saturated with the adsorbate (e.g. Pb) in the case of its intensive soil input, mainly of anthropogenic sources.

Table 1 lists some soil properties and amounts of Pb determined by three different extractants: Aqua regia, HNO<sub>3</sub> and DTPA. Soil particle size showed less variability, up to 35% whereas organic carbon ( $C_{\text{org}}$ ) and cation exchange capacity (CEC) varied by 43 and 63%, respectively. Amounts of Pb already present in the soils and extracted by the above-mentioned extractants, hereafter called correction values ( $CV$ ), varied notably from 61 to 78% thus indicating a differentiation of Pb levels in soils. These were in the interval 0.18 and 4.20 mmol<sub>c</sub>kg<sup>-1</sup> for Aqua regia. The dilute nitric acid (HNO<sub>3</sub>) extracted from 0.07 up to 2.93 mmol<sub>c</sub>kg<sup>-1</sup>. Exchangeable and organically bound Pb extracted by DTPA was comprised within 0.03 and 0.74 mmol<sub>c</sub>kg<sup>-1</sup>.

### a) Langmuir one-site uncorrected and corrected adsorption parameters

Because of its simplicity and the ability to calculate an adsorption maximum ( $a_{\max}$ ) and a relative bonding energy term ( $b$ ), the Langmuir equation has been used extensively to describe ion adsorption by soils and soil constituents. This equation applies for relatively smaller amounts of adsorbate and consequently at more dilute equilibrium concentrations. Table 2 presents uncorrected and corrected  $a_{\max}$  and  $b$  parameters. As could be observed, the parameters  $a_{\max}$  and  $b$  were inversely related: the higher the  $a_{\max}$  parameters the lower the  $b$  parameters. This is clearly shown for agricultural soils (AS: soils Nr 1, 2, 3). This finding seems to agree with the sorption theory reporting that mono as well as multilayers are usually formed with decreasing "retention" energy from the inner towards outer layers. The influence of correction values on  $a_{\max}$  and  $b$  parameters varied. For AS soils, rich in organic matter and with relatively high CEC, no marked differences for  $a_{\max}$  and  $b$  parameters were found, both for uncorrected and corrected parameters, irrespective of the correction value. These soils developed a great affinity for Pb as confirmed by  $a_{\max}$  parameters varying from 95.71 to 211.01 mmol<sub>c</sub>kg<sup>-1</sup>.

In the case of soils from the Glogow Sanitary Zone (GSZ: soils Nr 4, 5, 6, 7) poor in organic matter and consistently with low CEC and pH, the inclusion of the

Table 2. Changes of Langmuir one-site parameters without and with correction values.

Soil type (number)	uncorrected			Aqua regia			2 mol HNO <sub>3</sub>			DTPA <sub>(7.3)</sub>		
	<i>a</i> <sub>max</sub> <sup>*</sup>	<i>b</i> <sup>**</sup>	<i>r</i> <sup>***</sup>	corrected			corrected			corrected		
				<i>a</i> <sub>max</sub>	<i>b</i>	<i>r</i>	<i>a</i> <sub>max</sub>	<i>b</i>	<i>r</i>	<i>a</i> <sub>max</sub>	<i>b</i>	<i>r</i>
Loam (1)	211.01 (75.75) <sup>#</sup>	17.06 (4.39)	0.987	211.08 (72.71)	17.41 (4.07)	0.987	211.04 (73.21)	17.31 (4.71)	0.987	211.06 (75.01)	17.21 (7.08)	0.987
Loamy sand (2)	155.03 (46.18)	73.61 (29.69)	0.997	155.02 (45.94)	74.03 (29.98)	0.997	155.07 (46.12)	73.77 (29.78)	0.997	155.01 (46.12)	73.70 (29.72)	0.997
Sandy loam (3)	95.71 (24.75)	96.33 (29.27)	0.996	96.70 (20.08)	101.09 (30.89)	0.996	96.42 (21.52)	99.53 (30.39)	0.996	95.90 (23.72)	97.37 (30.20)	0.996
Loamy sand (4)	24.32 (4.97)	19.70 (2.65)	0.996	27.04 (3.51)	35.82 (9.24)	0.993	25.31 (3.42)	28.24 (6.48)	0.995	24.53 (4.13)	22.79 (3.15)	0.995
Sandy loam (5)	23.84 (4.02)	25.07 (3.45)	0.990	24.96 (3.09)	33.73 (6.28)	0.990	24.43 (3.22)	30.78 (3.22)	0.991	24.12 (3.38)	28.91 (4.39)	0.991
Sandy loam (6)	21.63 (4.66)	15.82 (2.37)	0.993	23.41 (2.01)	24.57 (2.71)	0.994	22.14 (2.74)	19.55 (2.74)	0.993	21.81 (3.71)	17.66 (2.42)	0.990
Sandy loam (7)	25.55 (2.09)	8.55 (0.58)	0.993	26.43 (2.25)	16.40 (2.49)	0.997	26.08 (1.78)	14.52 (1.78)	0.997	26.11 (1.39)	9.64 (0.48)	0.996

\* Adsorption maximum, (mmol<sub>c</sub>kg<sup>-1</sup>); \*\* Bonding energy term, (L mmol<sub>c</sub><sup>-1</sup>), \*\*\* Correlation coefficients (n = 10), <sup>#</sup> Standard deviation.

Table 3. Changes of Freundlich parameters without and with correction values.

Soil type (number)	uncorrected			Aqua regia			2 mol HNO <sub>3</sub>			DTPA <sub>(7.3)</sub>		
	<i>K</i> <sub>F</sub> <sup>a</sup>	<i>n</i> <sup>b</sup>	<i>r</i>	corrected			corrected			corrected		
				<i>K</i> <sub>F</sub>	<i>n</i>	<i>r</i>	<i>K</i> <sub>F</sub>	<i>n</i>	<i>r</i>	<i>K</i> <sub>F</sub>	<i>n</i>	<i>r</i>
Loam (1)	439.04 (107.38) <sup>#</sup>	0.552 (0.088)	0.986	435.01 (104.48)	0.544 (0.087)	0.986	437.04 (100.83)	0.548 (0.088)	0.986	438.09 (102.53)	0.549 (0.064)	0.986
Loamy sand (2)	540.03 (162.94)	0.498 (0.086)	0.930	538.08 (161.38)	0.492 (0.086)	0.930	539.04 (162.16)	0.493 (0.086)	0.930	540.03 (162.94)	0.494 (0.086)	0.930
Sandy loam (3)	240.01 (92.79)	0.396 (0.063)	0.951	233.02 (81.41)	0.381 (0.060)	0.953	234.09 (84.28)	0.385 (0.060)	0.954	238.12 (98.38)	0.393 (0.062)	0.952
Loamy sand (4)	46.97 (10.46)	0.521 (0.073)	0.976	39.67 (7.14)	0.326 (0.055)	0.996	41.08 (7.07)	0.399 (0.055)	0.989	44.07 (8.31)	0.472 (0.064)	0.982
Sandy loam (5)	43.52 (9.19)	0.467 (0.065)	0.962	39.31 (7.34)	0.368 (0.057)	0.977	40.27 (7.57)	0.398 (0.058)	0.973	41.11 (7.86)	0.420 (0.060)	0.972
Sandy loam (6)	34.11 (5.03)	0.489 (0.069)	0.986	31.30 (4.62)	0.340 (0.109)	0.994	32.12 (3.97)	0.415 (0.052)	0.991	32.92 (4.08)	0.450 (0.060)	0.989
Sandy loam (7)	48.16 (9.48)	0.648 (0.119)	0.969	40.03 (6.20)	0.443 (0.070)	0.985	40.90 (6.11)	0.481 (0.084)	0.983	46.18 (8.01)	0.613 (0.109)	0.972

<sup>a</sup> Freundlich partition parameter, (L kg<sup>-1</sup>); <sup>b</sup> constant (dimensionless), <sup>#</sup> Standard deviation.

correction values increased both *a*<sub>max</sub> and *b* parameters in comparison with uncorrected ones. The increments were more pronounced for the bonding energy terms than for maximum adsorption parameters. They were on average as follows:

uncorrected		Aqua regia		HNO <sub>3</sub>		DTPA	
<i>a</i> <sub>max</sub>	<i>b</i>	<i>a</i> <sub>max</sub>	<i>b</i>	<i>a</i> <sub>max</sub>	<i>b</i>	<i>a</i> <sub>max</sub>	<i>b</i>
100		+6	+60	+2	+34	+0.2	+14

where ”+” means an increment in relation to 100.

These relative values pertinently show the importance of soil Pb and its influence on *a*<sub>max</sub> and *b* parameters calculated for soils with relatively low CEC, organic matter content and additionally low pH. Since adsorption studies are generally carried out in the soil medium earlier enriched with the investigated adsorbate, therefore the possible direct impact of the given adsorbate on sorption processes should not be overlooked. In the case of the Langmuir one-site parameters a risk of underestimation will be unavoidable mainly for soils with low buffering capacities (low C<sub>org</sub>, CEC).

### b) Freundlich uncorrected and corrected adsorption parameters

Although the Freundlich equation has been rigorously and widely applied [21, 22], the goodness-of-fit of the Freundlich equation to adsorption data does not provide definitive information about the processes involved. This empirical equation generally applies to a wide range of equilibrium adsorbate concentration, but it is not possible to calculate either the adsorption maximum or bonding energy term as in the case of the Langmuir equation. Lead partition to the soil matrix was expressed by  $K_F$  and  $n$  parameters (Table 3). The correction values had influenced Freundlich sorption parameters and uncorrected ones were found to be relatively higher than the corrected ones, irrespective of the soil groups. The higher the correction values (in the case of Aqua regia) the lower the  $K_F$  and  $n$  and adversely for the DTPA.

In terms of relative values, the decrease observed for the corrected  $K_F$  in relation to the uncorrected ones for the GSZ soils is presented below:

Aqua regia		HNO <sub>3</sub>		DTPA	
uncorrected	corrected	uncorrected	corrected	uncorrected	corrected
$K_F$	$K_F$	$K_F$	$K_F$	$K_F$	$K_F$
100	-9	100	-6	100	-0.5

where "–" means a decrease in relation to 100.

It appears that the correction for soil Pb may decrease the partition parameter  $K_F$ . This situation was quite unexpected and one of the possible explanations could be that the insertion of the correction value into the model "simulated" a primary soil solid phase partition which,

theoretically, reduced the share of the next partition and so on. We can, therefore, assume on the basis of this theoretical approach that more Pb was partitioned to the soil matrix in the case without correction, and this resulted in higher  $K_F$  parameters than for correction. Agricultural soils retained several times more Pb than those of the sanitary zone. This could be attributed to the increase in sorptive properties due to the presence of an appreciable level of organic matter, developed CEC and also neutral soil medium.

### c) Gunary uncorrected and corrected adsorption parameter

Lead adsorption maximum parameters were calculated by using equations 4 and 5. The latter one, as it stands, clearly shows the direct dependence of the unique  $a_{max}$  parameters on lead equilibrium levels ( $C_e$ ). According to this isotherm, adsorption maximum is reached when  $C_e$  tends to infinity. This may be widely applicable for soils characterised by relatively low buffering properties and acidic conditions resulting in a great and consistent partition of lead to the soil aqueous phase. In such cases  $a_{max}$  parameters can be expected to be relatively low, as shown in Table 4 for GSZ soils. Otherwise, equilibrium state will be reached much later and the introduction of the root square  $\sqrt{C_e}$  to the denominator may "quadratically delay" the maximal Pb adsorption process. Lower  $a_{max}$  parameters may occur also in the following conditions:

- 1) when equilibration time is short, and
- 2) when soils have high sorptive capacities (e.g. agricultural soils).

Adsorption maximum parameters calculated for agricultural soils varied markedly, so parameters mentioned below represent only the GSZ soils.

Table 4. Changes of Gunary parameters without and with correction values.

Soil type (number)	uncorrected			Aqua regia			2 mol HNO <sub>3</sub>			DTPA <sub>(7.3)</sub>		
	$B$	$a_{max}^*$	$r$	corrected			corrected			corrected		
				$B$	$a_{max}$	$r$	$B$	$a_{max}$	$r$	$B$	$a_{max}$	$r$
Loam (1)	$3.5 \cdot 10^{-3}$	285.70 (34.57) <sup>#</sup>	0.968	$3.3 \cdot 10^{-3}$	303.08 (46.86)	0.971	$3.4 \cdot 10^{-3}$	294.11 (36.74)	0.969	$3.44 \cdot 10^{-3}$	290.78 (35.70)	0.969
Loamy sand (2)	$1.1 \cdot 10^{-2}$	91.09 (15.57)	0.808	$1.1 \cdot 10^{-2}$	91.03 (15.03)	0.812	$1.1 \cdot 10^{-2}$	91.01 (18.45)	0.809	$1.1 \cdot 10^{-2}$	91.02 (19.88)	0.808
Sandy loam (3)	$2.2 \cdot 10^{-2}$	45.52 (8.39)	0.855	$2.0 \cdot 10^{-2}$	50.00 (8.65)	0.889	$2.0 \cdot 10^{-2}$	50.04 (7.69)	0.880	$2.1 \cdot 10^{-2}$	46.69 (8.82)	0.864
Loamy sand (4)	$4.1 \cdot 10^{-2}$	24.46 (6.81)	0.970	$2.4 \cdot 10^{-2}$	41.77 (5.16)	0.998	$2.8 \cdot 10^{-2}$	35.78 (6.10)	0.996	$3.5 \cdot 10^{-2}$	28.66 (6.98)	0.987
Sandy loam (5)	$4.5 \cdot 10^{-2}$	22.21 (7.45)	0.965	$3.0 \cdot 10^{-2}$	33.33 (8.57)	0.993	$3.4 \cdot 10^{-2}$	29.49 (9.10)	0.989	$3.6 \cdot 10^{-2}$	27.81 (9.91)	0.985
Sandy loam (6)	$3.7 \cdot 10^{-2}$	27.06 (6.21)	0.991	$2.6 \cdot 10^{-2}$	38.52 (7.03)	0.999	$2.9 \cdot 10^{-2}$	34.51 (8.01)	0.997	$3.2 \cdot 10^{-2}$	31.30 (7.79)	0.995
Sandy loam (7)	$5.1 \cdot 10^{-2}$	19.62 (5.27)	0.995	$2.8 \cdot 10^{-2}$	35.79 (3.64)	0.998	$3.0 \cdot 10^{-2}$	33.35 (3.05)	0.998	$4.5 \cdot 10^{-2}$	22.24 (6.80)	0.996

\*  $a_{max} = 1/B$  (mmol<sub>c</sub>kg<sup>-1</sup>), # Standard deviation.

Table 5. Linear correlation coefficients between soil properties and unconnected or corrected Langmuir one-site sorption parameters (n = 7).

Feature	uncorrected		Aqua regia ( <i>Ar</i> )		2 mol HNO <sub>3</sub>		DTPA		
	corrected								
	<i>a</i> <sub>max</sub>	<i>b</i>	<i>a</i> <sub>max</sub>	<i>b</i>	<i>a</i> <sub>max</sub>	<i>b</i>	<i>a</i> <sub>max</sub>	<i>b</i>	
Clay	0.70**	-0.19	0.70**	-0.27	0.70**	-0.23	0.70**	-0.19	
C <sub>org</sub>	0.98****	0.47	0.98****	0.37	0.98****	0.41	0.98****	0.45	
CEC	0.99****	0.40	0.99****	0.28	0.99****	0.33	0.99****	0.37	
pH	0.89***	0.71**	0.89***	0.61**	0.89***	0.66**	0.89***	0.69**	
Pb	<i>Ar</i>	-0.79***	-0.60**	-0.79***	-0.46	-0.79***	-0.52*	-0.79***	-0.57*
	HNO <sub>3</sub>	-0.73**	-0.51*	-0.74**	-0.39	-0.74**	-0.44	-0.74**	-0.49*
	DTPA	-0.71**	-0.54*	-0.71**	-0.44	-0.72**	-0.48	-0.72**	-0.51*

\*, \*\*, \*\*\* and \*\*\*\* significant at P < 0.05, 0.01, 0.001 and 0.0001, respectively.

Table 6. Linear correlation coefficients between soil properties and unconnected or corrected Freundlich sorption parameter (n = 7).

Feature	uncorrected		Aqua regia ( <i>Ar</i> )		2 mol HNO <sub>3</sub>		DTPA		
	corrected								
	<i>K<sub>F</sub></i>								
Clay	0.45		0.45		0.45		0.45		
C <sub>org</sub>	0.97****		0.97****		0.97****		0.97****		
CEC	0.91****		0.91****		0.91****		0.91****		
pH	0.96****		0.96****		0.96****		0.96****		
Pb	<i>Ar</i>	-0.85***		-0.85***		-0.85***		-0.85***	
	HNO <sub>3</sub>	-0.83***		-0.83***		-0.82***		-0.83***	
	DTPA	-0.78***		-0.79***		-0.78***		-0.78***	

\*\*\* and \*\*\*\* significant at least at P < 0.001 and 0.0001, respectively.

Table 7. Linear correlation coefficients between soil properties and unconnected or corrected Guntary sorption parameter (n = 7).

Feature	uncorrected		Aqua regia ( <i>Ar</i> )		2 mol HNO <sub>3</sub>		DTPA		
	corrected								
	<i>a</i> <sub>max</sub>								
Clay	0.94****		0.93****		0.93****		0.94****		
C <sub>org</sub>	0.77***		0.77***		0.77***		0.77***		
CEC	0.86***		0.85***		0.86***		0.86***		
pH	0.90****		0.85***		0.86***		0.86***		
Pb	<i>Ar</i>	-0.52*		-0.50*		-0.51*		-0.51*	
	HNO <sub>3</sub>	-0.50*		-0.48		-0.49		-0.50*	
	DTPA	-0.38		-0.38		-0.38		-0.37	

\*, \*\*\* and \*\*\*\* significant at least at P < 0.05, 0.001 and 0.0001, respectively.

Aqua regia		HNO <sub>3</sub>	DTPA
uncorrected		corrected	
$a_{\max}$	$a_{\max}$	$a_{\max}$	$a_{\max}$
		%	
100	+60	+43	+18

where "+" means an increment in relation to 100.

The influence of correction values on  $a_{\max}$  parameters was similar to that reported earlier in the case of Langmuir one-site parameters. Gunary's  $a_{\max}$  parameters were higher than Langmuir ones in the order of 10, 22 and 90 times for Aqua regia, HNO<sub>3</sub> and DTPA, respectively. A striking similarity was observed for increments (in relative values) dealing with Langmuir bonding energy term  $b$ , and Gunary's  $a_{\max}$  parameters. A case hard to explain since the calculation of adsorption maximum limits any possible "insight" into the sorption processes. Furthermore, some additional difficulties arise when analysing Langmuir parameters calculated mainly for dilute solutions and Freundlich parameters obtained from a generally wide range of solutions (mostly less dilute solutions).

#### d) Uncorrected and corrected adsorption parameters versus soil properties

Lead sorption by soils is reported to be dependent on various factors among others pH, organic matter content as well as soil particles [23]. If sorption parameters may depend on any amount of lead in the soil there is a need for information on relationships between uncorrected and corrected sorption parameters and soil properties and, additionally, amounts of lead already present in soil (designated earlier as correction value). Tables 5, 6 and 7 list linear correlation coefficients for the Langmuir one-site, Freundlich and Gunary equations, respectively.

The inclusion or not of correction values during the calculation of Langmuir parameters did not exert any noticeable influence on the maximal amounts of lead adsorbed ( $a_{\max}$ ). Correlation coefficients for soil properties and  $a_{\max}$  (Table 5) were similar and significant, which could probably be attributed to the constant formation of the Pb monolayer irrespective of Pb level. Some variations were observed for bonding energy terms  $b$ , which gave markedly low correlation coefficients, mostly insignificant and predominantly for the relationships clay,  $C_{\text{org}}$ , CEC versus  $b$ , for both uncorrected and corrected cases. A slight and consistent increase of the correlation coefficients (even insignificant in some cases) with the inclusion of correction values in the order: Aqua regia > HNO<sub>3</sub> > DTPA may be a confirmation of the electrostatic attraction postulate. Soil properties and amounts of Pb determined by the particular extractants were differently correlated with adsorption parameters. Linear correlation coefficients for Langmuir  $a_{\max}$  versus soil properties (CEC, Corg., pH, and Clay), irrespective of the correction values may be ranked as follows:

$$\text{CEC (0.99*****)} > \text{Corg (0.98*****)} > \text{pH (0.89*****)} > \text{Clay (0.70**)} \quad (6)$$

where: \*\*, \*\*\* and \*\*\*\*\*: significant at  $P < 0.01$ , 0.001 and 0.0001, respectively; whereas  $a_{\max}$  versus Pb determined by the particular extractants yielded negative and all significant linear correlation coefficients:

$$\text{Ar}_{\text{Pb}} (-0.79****) > \text{HNO}_{3\text{Pb}} (-0.73**) > \text{DTPA}_{\text{Pb}} (-0.71**) \quad (7)$$

where: \*\* and \*\*\* significant at  $P < 0.01$  and 0.001, respectively; Ar-Pb, HNO<sub>3</sub>-Pb and DTPA-Pb: Aqua regia, HNO<sub>3</sub> and DTPA extracted Pb, respectively.

The Gunary  $a_{\max}$  were correlated with soil properties as in the case of Langmuir parameters, but linear correlation coefficients were found to be relatively low (except for  $a_{\max}$  versus clay,  $r > 0.93****$ ), as listed in Table 7. Organic carbon was weakly correlated with Gunary  $a_{\max}$  ( $r = 0.77***$ ), whereas almost similar relationships were found for both CEC and pH versus  $a_{\max}$ . The same pattern was found for Aqua regia, HNO<sub>3</sub> and DTPA extracted Pb versus uncorrected and corrected  $a_{\max}$  parameter, where correlation coefficients were negative and even insignificant in some cases.

Lead retention by the soil solid phase seemed to occur uniformly and no differences were observed between uncorrected and corrected Freundlich partition parameter  $K_F$  as shown in Table 6. Such lead sorption behaviour was earlier pointed out for the Langmuir and Gunary  $a_{\max}$ . The linear correlation coefficients ( $r$ ) of soil properties versus  $K_F$  were high and significant ( $0.91**** < r < 0.97****$ , for  $P < 0.0001$ ), except for clay with  $r = 0.45$ . Negative and relatively high linear correlation coefficients were obtained for extracted Pb and the  $K_F$  parameter and decreased in the order, irrespective of the extractant used:

$$\text{Ar-Pb (-0.85****)} > \text{HNO}_{3\text{-Pb}} (-0.83****) > \text{DTPA-Pb (-0.78****)} \quad (8)$$

where: \*\*\* significant at  $P < 0.001$ ; and Ar-Pb, HNO<sub>3</sub>-Pb and DTPA-Pb: Aqua regia, HNO<sub>3</sub> and DTPA extracted Pb, respectively.

Correlation coefficients obtained for correction values versus sorption parameters allowed to rank isotherms as follows: Freundlich > Langmuir > Gunary. This rank applies strictly for lead extracted by Aqua regia, HNO<sub>3</sub> and DTPA.

Correction for adsorbed Pb should be considered in sorption studies carried out mainly in media earlier enriched with Pb. The choice of an appropriate extractant for the "correction value" may depend both on the extractant feature and the sorbent type. Further studies on this topic are required to elucidate this state.

#### Appendix

$C_o$  - initial Pb concentration of the equilibrium solution, (mmol<sub>L</sub><sup>-1</sup>),

$C_e$  - equilibrium Pb concentration in the soil extracts, (mmol<sub>L</sub><sup>-1</sup>),

$CV$  - amount of Pb already present in the soils (= correction value), (cmol<sub>kg</sub><sup>-1</sup>),

$S$  - amount of Pb adsorbed, ( $\text{mmol}_c\text{kg}^{-1}$ ),  
 $a_{\text{max}}$  - adsorption maximum, ( $\text{mmol}_c\text{kg}^{-1}$ ),  
 $b$  - bonding energy term, ( $\text{L mmol}_c^{-1}$ ),  
 $V$  - volume of the equilibrium solution, (L),  
 $W$  - weight of soil sample, (kg),  
 $K_F$  - Freundlich partition parameter, ( $\text{L kg}^{-1}$ ),  
 $n$  - Freundlich constant (dimensionless),  
 $A, B, D$  - Gunary's adsorption constants,  
 GSZ - Glogow Sanitary Zone  
 AS - Agricultural soils

## References

- ADRIANO, D. C, Trace Elements in the Terrestrial Environment. Springer-Verlag, New York, **1986**.
- BASTA N. T., TABATABAI M. T, Effect of cropping system on adsorption of metals by soils: 1. Single-metal adsorption. *Soil Sci.* **153**, 108, **1992**.
- KABATA-PENDIAS A., Behavioral properties of traces metals in soils. *Applied Geochemistry. Suppl. Issue*, **2**, pp. 2-9, **1993**.
- YANAI J., YABUTANI M, YAMEI K., BIAO H., GUOBAO L., KOSAKI T., Heavy metal pollution of agricultural soils and sediments in Liaoning province, China. *Soil Sci. Plant Nutr.* **44(3)**, 367, **1998**.
- GAMBUS F., The applicability of the Langmuir and Freundlich equations to describe copper sorption in the soil depending on its pH and granulometric composition. *Pol. Jour. Soil Sci.*, Vol. **XX/2**, 11, **1987**.
- JORGENSEN S. S., WILLEMS M., The fate of lead in soils: The transformation of lead pellets in shooting-ranges soils. *Ambio.* **16**, 11, **1987**.
- OLSEN S. R., WATANABE F. S., A method to determine a phosphorus adsorption maximum of soil as measured by the Langmuir isotherm. *Soil Sci. Soc. Pro.* **21**, 144, **1957**.
- NYCHAS A. E., Phosphate sorption by Greek alkaline soils evaluated with a modified Freundlich equation. *Z. Pflanzenernaehr. Bodenk.* **145**, 593, **1982**.
- ASSIMAKOPOULOS I, KOSMAS C, NYCHAS A, BOVIS C, The effect of previous P additions on sorption indices of calcareous soils determined with commonly employed methods. *Z. Pflanzenernaehr. Bodenk.* **149**, 548, **1986**.
- SIBBESEN E., Some new equations to describe phosphate sorption by soils. *Journal of Soil Science* **32**, 64, **1981**.
- GUNARY D., A new adsorption isotherm for phosphate in soil. *Jour, of Soil Science*, **21** (1), 73, **1970**.
- DIATTA J. B, KOCIALKOWSKI W. Z., Adsorption of zinc in some selected soils. *Polish Jour, of Envir. Stud.* **7** (4), 195, **1998**.
- KOCIALKOWSKI W. Z., DIATTA J. B., GRZEBISZ W., Assessment of lead sorption by acid agroforest soils. *Polish Jour, of Envir. Stud.* **8** (6), 403, **1999**.
- LITYNSKI T., JURKOWSKA H., GORLACH E., Analiza-chemiczno-rolnicza. PWN, Warszawa, **1976**.
- Polska Norma: Polski Komitet Normalizacyjny, nr ref. PrPN-ISO 10390 (E), Jakosc gleby i oznaczanie pH. Pierwsze wydanie, **1994**.
- KOCIALKOWSKI W. Z., RATAJCZAK M. J., Uproszczona metoda oznaczania kationow wymiennych i pojemnosci wymiennej w stosunku do kationow wedlug metody Roczn. AR- Poznan; CXLVI, 106-116 (with summary in english), **1984**.
- SAUERBECK D., LUBBEN S., Okologie ein Forder-schwerpunkt des BMFT. **6**, **1991**.
- ANDERSSON A., Relative efficiency of nine different soil extractants. *Swedish J. Agric. Res.* **5**, 125, **1975**.
- LINDSAY W. L., NORVELL W. A. Development of a DTPA soil test for zinc, iron, manganese and copper. *Soil Sci. Soc. Am. J.* **42**, 421, **1978**.
- SALIM I. A, MILLER C. J, HOWARD C. J, Sorption isotherm-sequential extraction analysis of heavy metal retention in landfill liners. *Soil Sci. Soc. Am. J.* **60**, 107, **1996**.
- BOWMAN B. T., Conversion of Freundlich adsorption lvalues to the mole fraction format and the use of  $S_v$  values to express relative adsorption of pesticides. *Soil Sci. Soc. Am. J.* **46**, 740, **1982**.
- BUCHTER B, DAVIDOFF B., AMACHER M. C, HINZ C, ISKANDAR I. K., SELIM H. M., Correlation of Freundlich  $K_d$  and  $n$  retention parameters with soils and elements. *Soil Sci.*, **148** (5), 370, **1989**.
- MCBRIDE: Reactions controlling heavy metal solubility in soil. *Advances in Soil Science. Springer-Verlag New York Inc* Vol. **10**, 1, **1989**.