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APPLICATION OF THE PARTITION COEFFICIENT FOR ASSESSING HEAVY METALS MOBILITY WITHIN THE MIASTECZKO SLASKIE ZINC SMETLER IMPACT ZONE (POLAND)

ZASTOSOWANIE WSPÓŁCZYNNIKA PODZIAŁU DO OCENY RUCHLIWOŚCI METALI CIĘŻKICH W STREFIE ODDZIAŁYWANIA HUTY CYNKU W MIASTECZKU ŚLĄSKIM (POLSKA)

Abstract: The present paper outlines some approaches, which were suggested for assessing heavy metals (Cu, Zn, Pb and Cd) mobility in soils contaminated by a zinc smelter activity. The concept was based on the assumption that partition coefficients, as ratios of total (assayed by *aqua regia*) metal contents to exchangeable (extracted by 1 mol $CH_3COONH_4 \cdot dm^{-3}$, pH 7.0) or to bioavailable (extracted by 0.1 mol $NaNO_3 \cdot dm^{-3}$) metal contents, will be more predictive in assessing metals mobility as compared with single extractions. The calculated partition coefficients for exchangeable and bioavailable metal forms were respectively termed K_d-Ex and K_d-Bio, which in turn were intended to represent the *statico-dynamic* nature of heavy metal mobility.

It was found that metal mobility followed the sequence Cd > Zn > Pb > Cu, which implies that Cd and Zn will evoke more threat due to greater susceptibility for mobility. Regressions for the pairs $\log K_d$ *versus* pH were applied in order to exhibit the proton generating capacity of each metal. The average calculated proton coefficient in the case of exchangeable metal forms amounted to 0.16 mole of protons released for each mole of Cu, Zn and Pb. In contrast, the proton coefficient for Cd was about 81 % greater. The estimation made on the basis of bioavailable metal forms showed, that Cd and Zn retention by soils generated, respectively 77 and 131 % more protons as compared to Pb. In terms of environmental concern, it may be formulated, that the higher the proton generating capacity, the highest the metal mobility, and thus the weakest partition to the solid phase.

Keywords: partition coefficient, exchangeable, bioavailable forms, copper, zinc, lead, cadmium, zinc smelter

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Heavy metals, including micronutrients and toxic metals, exhibit a high affinity for naturally occurring adsorbents and the reactions between these metal ions and the adsorbents are observed to be weakly reversible. The magnitude of this process is generally estimated by chemical tests as well as speciation studies [1–3]. The mobility of heavy metals in contaminated soils is a notion of *static* nature (application of different chemical tests for heavy metals extractions), of *dynamic* nature (phytotests, batch studiem) and *statico-dynamic nature* (partition coefficients relating the content of heavy metals in the soil solid phase and soil solution concentration). The ratio of metals in the solid phase to those in solution at equilibrium is defined as partition coefficient K_d, which is reported as M_{ads}/M_{sol} where, M_{ads} – adsorbed/retained metal and M_{sol} – metal in solution [4–6]. High values of the partition coefficient are believed to indicate that metals have been retained by the soil solid phase through sorption reactions, while low values imply that most of metals are partitioned to the ambient soil solution, where they are potentially prone to transport and biological or geochemical reactions. The involved mechanisms are related to several physical and chemical soil properties of which soil reaction (pH), organic matter, clay and silt contents are mostly considered to control dynamic processes of metal geochemistry [7]. Therefore it seems targeted to apply the partition coefficient for assessing metal mobility, since this parameter involves intrinsically the buffering capacity, a core soils geochemical feature [8, 9].

The concept of the present paper is based on the assumption that bioavailable (assayed by 0.1 mol $NaNO_3 \cdot dm^{-3}$) and exchangeable (extracted by 1 mol $CH_3COONH_4 \cdot dm^{-3}$) metal fractions express a *static* approach in terms of metals mobility. The consideration of the partition coefficient (K_d) in assessing the potential mobility of these metal fractions in contaminated as well as polluted soils will provide more details, since the evaluation shifts from the *static* towards the dynamic approach ie, *statico-dynamic* nature of metal mobility-based processes.

The purpose of the paper is to outline some approaches in the evaluation of the partition coefficients-based heavy metals mobility in soils subjected to contamination by a Zinc Smelter activity.

Materials and methods

Location of the research area

The research area lies within the impact zone of the Miasteczko Slaskie Zinc Smelter, (N $51^o41'03''$ and E $15^o57'12''$, Poland) whose activity started since 1966. This zone is surrounded in the north, west and east by a large Lubliniec Forest complex, and in the south-east by the localities of Zyglin and Zygliniec, quarters of the Miasteczko Slaskie. A population of pine as part of artificial restoration, mainly of mixed forest, sporadically mixed wood grows in the impact zone. In the Miasteczko Slaskie region, the prevailing winds are from the south-westerly (21.4 %) and westerly (18.7 %) quarters, hence the emitted pollutants create the greatest threat to areas in the north-east and east zones of the Zinc Smelter.

Sample collection and analytical procedures

Five samples ordered like the five on a dice, with 15 m distance from the central point were collected (20 cm depth) at 8 selected sites (Table 1) on June, 2006.

Table 1

Selected physical and chemical properties of soils in the impact zone
of the Miasteczko Slaskie Zinc Smelter (mean, n = 5)

Site	Particles [g · kg^{-1}]		$C_{org.}$ [g · kg^{-1}]	EC [μS · cm^{-1}]	pH 0.01 mol CaCl$_2$ · dm^{-3}	Ca	CEC
	Silt	Clay				[cmol(+) · kg^{-1}]	
A	90	90	5.5	34.7	5.7	1.0	1.4
B	150	90	9.1	41.6	4.9	1.4	1.8
C	490	260	15.5	189.0	7.2	24.1	26.8
D	240	260	20.0	128.5	7.5	13.3	15.1
E	270	130	11.2	68.3	5.6	4.3	5.4
F	290	80	7.5	72.3	6.0	4.9	5.9
G	410	90	31.1	65.7	4.6	2.2	2.9
H	180	60	66.4	134.6	3.4	1.8	2.5

Explanation: A, B – Experimental area 500 and 1100 m ESE, respectively; C – Cynkowa Street, 100 m SE from the Zinc Smelter (Miasteczko Slaskie); D – Dworcowa Street, 500 m W from the Zinc Smelter (Miasteczko Slaskie); E – Brynicka Street, 500 m E from the Zinc Smelter (Zyglin) F – Sw. Marka Street, 1500 m SE from the Zinc Smelter (Zyglin); G – Zyglinska Street, 4500 m E from the Zinc Smelter (Brynica); H – Staromiejska Street, 6000 m E from the Zinc Smelter (Bibiela); EC – Electrical Conductivity; CEC – Cation Exchange Capacity.

Prior to basic analyses soil samples were air-dried and crushed to pass through a 1 mm sieve. Granulometric composition was determined by the areometric method [10] and organic carbon by the Walkley-Black method as reported by Nelson and Sommers [11]. Soil pH at soil/solution ratio of 1:5 (0.01 mol CaCl$_2$ · dm^{-3}) was determined potentiometrically using a pH-meter [12], whereas the electrical conductivity was assayed in water extracts according to Jackson [13]. The cation exchange capacity (CEC) was obtained by summation of 1 mol KCl · dm^{-3} extractable acidity and exchangeable alkaline cations (Ca^{2+}, Mg^{2+}, Na$^+$ and K$^+$) extracted by 1 mol CH$_3$COONH$_4$ · dm^{-3} (pH 7.0) as described by Thomas [14]. The total content of heavy metals was determined by using the *aqua regia* procedure [15], whereas the bio-available as well as exchangeable metals forms were assayed by 0.10 mol NaNO$_3$ · dm^{-3} [16] and 1 mol CH$_3$COONH$_4$ · dm^{-3} (pH 7.0) [17], respectively. All performed chemical tests were run in duplication and metals as well as other elements were determined by the FAAS method (*Flame Atomic Absorption Spectrophotometry*, Varian 250 plus). Computations and statistical evaluations were made by using the Excel® sheet.

Results and discussion

Soil properties versus exchangeable and bioavailable heavy metal content

Soils within the impact zone of the Miasteczko Slaskie Zinc Smelter are characterized by significantly different physical and chemical properties, summarized in Table 1. Soil reaction (pH) varied broadly from very acidic (pH_{CaCl_2} = 3.4) at the site H to slightly alkaline (pH = 7.5) for soils of the site D. Organic carbon (C_{org}) content fluctuated within a large range, ie, 5.5–66.4 g · kg^{-1}, whereas the cation exchange capacity (CEC) was in most cases markedly low (from 1.4 to 5.9 cmol(+) · kg^{-1}), except for sites C and D with CEC values of 26.8 and 15.1 cmol(+) · kg^{-1}, respectively. The amount of silt and clay fractions reveals that investigated soils are preponderatingly sandy, ca 75 % of soils exhibited silt + clay < 500 g · kg^{-1}. Such a soil texture may create a serious threat due to strengthened pollutants migration downward. The mean heavy metals content as reported in Table 2 showed significant variations related most specifically with both sites and type of metal.

Table 2

Total (*aqua regia*) metal contents within the impact zone
of the Miasteczko Slaskie Zinc Smelter (mean ± SD, n = 5)

Site	Cu	Zn	Pb	Cd
	[mg · kg^{-1}]			
A	5.15 ± 0.45	614.50 ± 30.43	404.15 ± 46.96	5.75 ± 1.16
B	5.40 ± 1.29	368.50 ± 39.47	542.15 ± 61.44	5.05 ± 1.08
C	69.60 ± 12.40	4832.0 ± 517.48	2986.0 ± 147.88	52.00 ± 5.82
D	56.55 ± 9.69	1351.8 ± 247.69	1009.65 ± 95.60	16.35 ± 2.45
E	6.60 ± 0.80	246.0 ± 31.10	352.15 ± 14.65	5.52 ± 0.38
F	6.20 ± 1.36	649.0 ± 88.56	226.95 ± 12.34	5.05 ± 0.84
G	5.00 ± 0.40	202.0 ± 7.62	288.10 ± 24.04	4.50 ± 0.47
H	5.95 ± 0.86	240.0 ± 31.42	446.15 ± 30.35	4.35 ± 0.78
BLP	17.5	75.0	40.0	0.65

Explanation: SD – Standard deviation; Site – see Table 1; BLP – Background Level for Poland [18].

In the case of Zn, Pb and Cd, their levels exceeded ca 3 to 64 times; 6 to 75 times and 7 to 80 times, respectively, the Background Level for Poland (BLP) [18], (Table 2), in opposite to Cu with 75 % of its content not exceeding the BLP value. These orders of magnitude clearly show that cadmium and lead are the most threatening heavy metals in the impact zone. Zinc in turn occupies the intermediate position.

Linear correlation coefficients (only r ≥ 0.50 were considered) established for the pairs: soil properties (ie, CEC, Clay + silt, C_{org} and pH) *versus* exchangeable and bioavailable forms of Cu, Zn, Pb and Cd (Table 3) have outlined the occurrence of two groups of factors as determinants of metals geochemical dynamics of soils within the impact zone.

Table 3

Exchangeable (*Ex*) and bioavailable (*Bio*) Cu, Zn, Pb and Cd concentrations
within the impact zone of the Miasteczko Slaskie Zinc Smelter (mean, n = 5)

Site	Cu		Zn		Pb		Cd	
	Ex	*Bio*	*Ex*	*Bio*	*Ex*	*Bio*	*Ex*	*Bio*
	$[mg \cdot dm^{-3}]$							
A	0.034	t	19.71	14.25	3.63	0.424	0.212	0.568
B	0.025	t	10.13	13.83	7.11	0.129	0.175	0.410
C	0.086	t	16.77	10.65	7.33	0.304	0.386	0.257
D	0.046	t	15.04	6.33	6.30	0.049	0.292	0.093
E	0.022	t	3.74	2.09	0.33	0.071	0.073	0.064
F	0.027	t	4.96	1.15	1.09	0.062	0.066	0.060
G	0.023	t	1.65	0.15	0.70	0.065	0.045	0.062
H	0.024	t	2.90	0.22	2.56	0.074	0.056	0.074

Explanation: Site – see Table 1; *Ex* – extracted by 1.0 mol $CH_3COONH_4 \cdot dm^{-3}$, pH 7.0 (ratio *w:v* = 1:10);
Bio – extracted by 0.10 mol $NaNO_3 \cdot dm^{-3}$ (ratio *w:v* = 1:2); t – traces (below detection limit).

These are the CEC and pH for exchangeable forms, with correlation coefficients (r) varying within the range: $0.62 \leq r \leq 0.86$, (p < 0.01). Organic carbon (C_{org}) content and pH were found to be the most significant determinants for bioavailable forms, since correlation coefficients fluctuated accordingly: $0.53 \leq r \leq 0.75$, (p < 0.01). This implies that the mobility of metals within the investigated ecosystem may be high due to decomposition of organic matter in one hand and to soil pH, which is potentially instable. More analyses are required to confirm such effects in detail, especially with respect to the activities of the soil microflora.

Partition coefficient, metal mobility estimation

The values of the partition coefficients (Table 4) varied widely accordingly to the particular metals and also depending on the chemically extracted metal forms (ie, extractable and bioavailable). Of these values, K_d-*Ex* for Cu as well as K_d-*Bio* both for Zn and Pb the most, spanned the widest ranges. On the basis of mean K_d values the following sequences may be established:

$$K_d\text{-}Ex: \quad \text{Cu} > \text{Pb} > \text{Zn} > \text{Cd}$$
$$K_d\text{-}Bio: \quad \text{Pb} > \text{Zn} > \text{Cd}$$

Interestingly the reported sequences follow the same trends, which implies that buffering capacities developed by soils within the impact zone control similarly exchangeable as well as bioavailable metals. This is particularly important in terms of mobility evaluation. The latter one follows the reverse sequence, ie, Cu < Pb < Zn < Cd,

which points out at the higher mobility of Cd and Zn over Pb and Cu as reported by Matos et al [19]. This is in line with the electronegativity of these metals and additionally with data reported by Christophi and Axe [20] and Fontes et al [21].

Table 4

Exchangeable (*Ex*) and bioavailable (*Bio*)-based partition coefficients (K_d) calculated for Cu, Zn, Pb and Cd

Heavy metals	Description	K_d-Ex	K_d-Bio
		$[dm^3 \cdot kg^{-1}]$	
Cu	R	154.2–1446.1	t
	M (*SD*)	465.5 (*143.7*)	t
Zn	R	31.3–288.6	14.6–4365.4
	M (*SD*)	106.5 (*13.4*)	1427.9 (*379.1*)
Pb	R	88.0–589.3	689.4–47869.8
	M (*SD*)	276.2 (*64.6*)	11643.0 (*2718.8*)
Cd	R	27.3–134.5	6.1–884.8
	M (*SD*)	72.8 (*12.7*)	176.3 (*33.0*)

Explanation: K_d-Ex – based on the ratio of total metal content (*Aqua regia*) to exchangeable metal content (*1 mol $CH_3COONH_4 \cdot dm^{-3}$, pH 7.0*); K_d-Bio – based on the ratio of total metal content (*Aqua regia*) to bioavailable metal content (*0.10 mol $NaNO_3 \cdot dm^{-3}$*); R – range, M(SD) – mean (n = 40) and standard deviation; t – traces (below detection limit).

A stepwise regression analysis was used to develop empirical models to estimate K_d for each metal. The relevant equations are reported below:

For exchangeable metal forms, K_d-Ex for:
Cu = 312.8 · pH + 91.9 · C_{org} − 1474.9; $R^2 = 0.52$
Zn = −24.2 · pH + 10.2 · CEC + 163.9; $R^2 = 0.71$
Pb = 3.70 · Clay + Silt + 133.5; $R^2 = 0.17$
Cd = 1.08 · Clay + Silt + 31.9; $R^2 = 0.43$

For bioavailable metal forms, K_d-Bio for:
Zn = −208.6 · C_{org} + 110.9 · CEC + 991.2; $R^2 = 0.41$
Pb = 1518.8 · CEC − 82.9; $R^2 = 0.75$
Cd = 30.8 · CEC − 61.7; $R^2 = 0.86$

Although the coefficients of determination-based equations reported just above are useful for estimating the *statico-dynamic* nature of K_d, they are predictive only. They are not intended to describe adsorption mechanisms or even the relative contribution of the individual soil components to the adsorption/retention processes. In addition, if these equations are to be used to predict values of K_d, three or four characteristics must be specified for each soil considered. Clearly a simpler method for evaluating K_d-based

metal mobility would be useful. Therefore, consider the simplified metal sorp-tion/retention reaction:

$$S - H_\alpha + M^{2+} \rightarrow S - M + \alpha H^+ \tag{1}$$
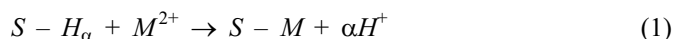
where: $S - H_\alpha$ – represents the surface binding sites,
M^{2+} – represents soluble metal species,
$S - M$ – represents surface-bound metal,
α – the proton coefficient represents the number of protons released when the metal binds.

An equilibrium constant can be rewritten for reaction (1) as:

$$K = \frac{(S-M) \cdot (H)^\alpha}{(M) \cdot (S-H)} \tag{2}$$

Substituting and solving for K_d in the logarithmic form yields the expression:

$$\log K_d = \alpha pH \, \log K \cdot (S - H) \tag{3}$$

A similar mass action approach was outlined by Kurbatov et al [22], and Honeyman [23] has discussed the limitations of this approach including the requirement for an excess of surface binding sites and the dependence of proton released on system pH.

In the present study we have assumed there was an excess of surface binding sites for each soil. If this is true and the site concentrations among the various soils are not significantly different, Eq. (3) would be valid not just for each soil independently, but for all soils, considered together. To test this assumption, exchangeable metals (Cu, Zn, Pb and Cd) extracted by 1 mol $CH_3COONH_4 \cdot dm^{-3}$, pH 7.0 as well as bioavailable ones, extracted by 0.10 mol $NaNO_3 \cdot dm^{-3}$ were plotted according to Eq. (3). The resulting slopes of the lines (Fig. 1) give a proton coefficient, which is an average over the soil pH ranges for the number of protons potentially generated by metals persistence in these sites (ie, contaminated soils).

The scatter in Fig. 1 may result because an equivalent concentration of high energy binding sites were not present in each of the soils. The stepwise correlations suggest that some of the most important sites involve the clay + silt pool and C_{org}. In soils characterized by low levels of these components, metals would be partitioned to lower energy binding sites, resulting in different parameters for Eq. (3).

The average calculated proton coefficient in the case of exchangeable metal forms amounts to 0.16 mol of protons released for each mole of Cu, Zn and Pb. In contrast, the proton coefficient for Cd is ca 81 % greater. The estimation made on the basis of bioavailable metal forms shows that Cd and Zn retention by soils has been generating 77 and 131 % more protons, respectively, as compared to Pb. The proton generating capacity of Zn was reported earlier by Leckie et al [24], who found that the retention of Zn produced ca 75 % more H^+ compared to Cd, Cu and Pb, whereas Anderson and Christensen [4] reported a value of 40 % for Zn with respect to Cd, Co and Ni. These
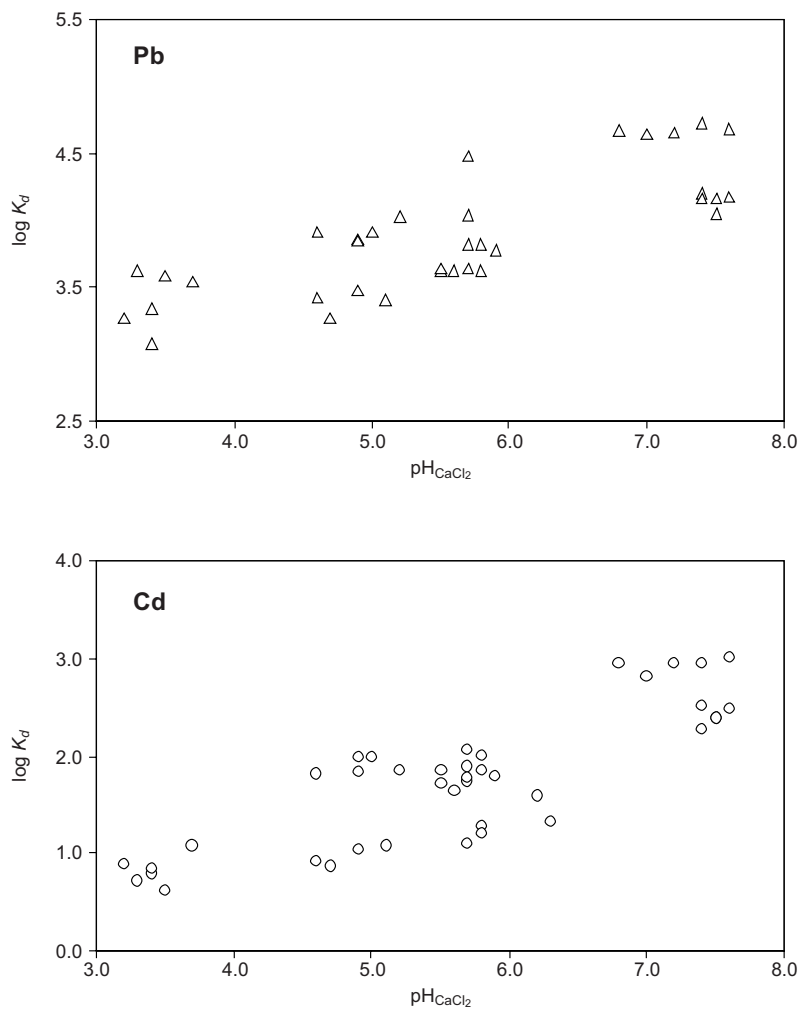
Fig. 1. Log K_d for bioavailable Pb and Cd as a function of pH

results suggest that for some surfaces, the sites involved in Zn and Cd retention in investigated soils are different from the sites involved for other metals. If these Zn and Cd binding sites are relatively more abundant, the assumptions made in developing these equations are more appropriate for Zn and Cd than for Cu and Pb. The equation also indicates that the partition coefficients for Zn and Cd are more sensitive to fluctuations in pH. In the event of reduced soil pH, Zn and Cd mobility would increase more rapidly than the other metals.

Heavy metals geochemistry is specifically related with protons generation, which in turn tend to lower the soil pH in order to increase solution metals activity. A sum up of data for all metals is reported in Table 5.

Table 5

Best values for proton coefficients (α) and intercepts for estimating $\log K_d$ from Eq. (3)

Metal	Partition coefficient	α [mol protons per mol of metal]	Intercept	R^2	n
Cu		0.18 ± 0.12	1.58	0.68	39
Zn	K_d-Ex	0.12 ± 0.05	1.46	0.47	36
Pb		0.18 ± 0.11	1.09	0.52	37
Cd		0.29 ± 0.01	0.02	0.64	37
Cu		nc	nc	nc	nc
Zn	K_d-Bio	0.60 ± 0.12	-1.34	0.79	38
Pb		0.26 ± 0.14	2.42	0.73	39
Cd		0.46 ± 0.11	-0.82	0.74	40

R^2 – coefficient of determination; n – number of samples, obvious outliers have been deleted; nc – not calculated (see Table 4: K_d-Bio).

Conclusions and statements

The consideration of the partition coefficient (K_d) in assessing the potential mobility of Cu, Zn, Pb and Cd in contaminated as well as polluted soils has revealed the intrinsic necessity for involving soil physical and chemical properties. This approach provided more details, which in turn set the basis of the *statico-dynamic* nature of metal mobility-based processes. Although the coefficients of determination-based equations were useful for estimating the *statico-dynamic* nature of K_d, they were predictive only. They were not intended to describe adsorption mechanisms, or even the relative contribution of the individual soil components to the adsorption/retention processes. Therefore $\log K_d$ *versus* pH regressions were applied in order to exhibit the proton generating capacity of each metal. The average calculated proton coefficient in the case of exchangeable metal forms amounted to 0.16 mol of protons released for each mol of Cu, Zn and Pb. In contrast, the proton coefficient for Cd was ca 81 % greater. The estimation made on the basis of bioavailable metal forms showed that Cd and Zn retention by soils generated, respectively 77 and 131 % more protons as compared to Pb. In terms of environmental concern, it may be formulated that the higher the proton generating capacity, the highest the metal mobility, and thus the weakest partition to the solid phase.

Acknowledgments

References

[1] Lebourg A., Sterckeman T., Ciesielski H. and Proix N.: Agronomie 1996, **16**, 201–215.
[2] Kociałkowski W., Diatta J. B. and Grzebisz W.: Polish J. Environ. Stud. 1999, **8**(3), 149–154.
[3] Al-Turki A.I. and Helal M.I.D.: Pakistan J. Biol. Sci. 2004, **7**(1), 1972–1980.
[4] Anderson P.R. and Christensen T.H.: J. Soil Sci. 1988, **39**, 15–22.
[5] Gooddy D.C., Shand P., Kinniburgh D.G. and Van Riemsdijk W.H.: Eur. J. Soil Sci. 1995, **46**, 265–285.
[6] Yuan G.: Commun. Soil Sci. Plant Anal. 2003, **34**(15–16), 2315–2326.
[7] Han F.X., Banin A., Kingery W.L., Triplett G.B., Zhou L.X., Zheng S.J. and Ding W.X.: Adv. Environ. Res. 2003, **8**, 113–120.
[8] Christensen T.H., Astrup T., Boddum J.K., Hansen B.Ø. and Redemann S.: Water Res. 2000, **34**(3), 709–712.
[9] Diatta J.B., Kociałkowski W.Z. and Grzebisz W.: Commun. Soil Sci. Plant Anal. **34**(17–18), 2419–2439.
[10] Gee G.W. and Bauder J.W.: [in:] Methods of Soil Analysis. Part 1. Physical and Mineralogical Methods, 2nd Edition, Klute A. (ed.), Agron. Monogr. 9 ASA and SSSA, Madison, WI, 1986, p. 383–411.
[11] Nelson D.W. and Sommers L.E.: [in:] Methods of Soil Analysis. Part 3. Chemical Methods, Sparks D.L. (ed.), SSA Book Ser. 5, 1986, pp. 961–1010, SSSA, Madison, WI.
[12] Polish Standard, Polish Standardisation Committee, ref. PrPN-ISO 10390 (E): Soil quality and pH determination. First edition, 1994 (in Polish).
[13] Jackson M.L.: Soil chemical analysis, Prentice-Hall, Inc. Englewood Cliffs, N.J. 1958.
[14] Thomas G.W.: [in:] Methods of Soil Analysis, Part 2. Chemical and Microbial Properties. 2nd Edition, Page A.L, Miller R.H. and Keeney D.R. (eds.), No. 9, ASA-SSSA, 1982, p. 159–165, Madison, Wisconsin, USA.
[15] International Standard: Soil Quality – Extraction of trace elements soluble in aqua regia. ISO 11466, Geneva 1995.
[16] Gupta S.K. and Hani H.: Rapport final COST 681, No. 2, (FAC), 1989.
[17] Anderson A.: Swedish J. Agric. Res. 1975, **5**, 125–135.
[18] Kabata-Pendias: Heavy metals in soils – issues in Central and Eastern Europe. International Conference, Hamburg 1995, **1**, 20–27.
[19] Matos A.T., Fontes M.P.F., Jordao C.P. and da Costa L.M.: Rev. Brasil. Ciencia do Solo 1996, **20**, 379–386.
[20] Christophi A.C. and Axe L.: J. Environ. Eng. 2000, **126**(1), 66–74.
[21] Fontes M.P.F., de Matos A.T., da Costa L.M. and Neves J.C.L.: Commun. Soil Sci. Plant Anal. 2000, **31**, 2939–2958.
[22] Kurbatov M.H., Wood G.B. and Kurbatow J.D.: J. Phys. Chem. 1951, **55**, 1170–1182.
[23] Honeyman B.D.: Ph.D. thesis, Stanford University, Stanford, CA, USA, 1984.
[24] Leckie J.O., Benjamin M.M., Haynes K., Kaufaman G. and Altmann S.: CS-1513. Research Project 910–1. Electric Power Research Institute, Palo Alto, CA, USA.

ZASTOSOWANIE WSPÓŁCZYNNIKA PODZIAŁU
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Abstrakt: Praca przedstawia zagadnienia związane z oceną ruchliwości metali ciężkich (Cu, Zn, Pb, Cd) w glebach zanieczyszczonych w wyniku działalności huty cynku. Koncepcja opierała się na założeniu, że współczynniki podziału jako stosunki całkowitej zawartości metali (oznaczonej w wodzie królewskiej) do zawartości wymiennych (ekstrahowanych przez 1 mol $CH_3COONH_4 \cdot dm^{-3}$, pH 7.0) lub do zawartości biodostępnych (ekstrahowanych przez 0.10 mol $NaNO_3 \cdot dm^{-3}$) metali są bardziej przydatne do prognozowania ruchliwości metali ciężkich niż w przypadku pojedynczych ekstrakcji. Obliczone współczynniki

podziału przyjęto odpowiednio jako K_d-Ex i K_d-Bio, które z kolei miały odzwierciedlić *statyczno-dynamiczny* charakter ruchliwości metali ciężkich.

Uzyskane wyniki przedstawiają szereg Cd > Zn > Pb > Cu, z którego wynika, że Cd i Zn stanowią większe zagrożenie z uwagi na większą ich ruchliwość w glebie. Zależności między log K_d a pH wykorzystano w celu obliczenia zdolności każdego metalu do generowania jonów wodorowych. Średnie wartości obliczone dla wymiennych form metali wynosiły 0.16 mola protonów uwolnionych na każdy mol Cu, Zn i Pb w odróżnieniu od Cd, dla którego wartość ta była o 81 % większa. Oszacowanie dokonane na podstawie zawartości biodostępnych form metali ujawniło, że zatrzymywanie Cd i Zn przez gleby spowodowało generowanie odpowiednio o 77 i 131 % więcej protonów w porównaniu z Pb. Biorąc pod uwagę zagrożenie przyrodnicze, należy przyjąć, że im większa zdolność do generowania protonów, tym większą ruchliwość wykazuje dany metal i tym samym słabsze jest jego zatrzymywanie przez fazę stałą gleby.

Słowa kluczowe: współczynnik podziału, wymienne, biodostępne formy, miedź, cynk, ołów, kadm, huta cynku