

Copper Distribution and Quantity-Intensity Parameters of Highly Contaminated Soils in the Vicinity of a Copper Plant

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Abstract

Four soil samples were collected in areas adjacent (*sanitary zone*) to the Gtgow Copper Plant in Poland. They were mostly acidic (pH 4.55 - 4.71) and the total varied widely in their total copper content from 17.03 to 44.07 cm_o/kg . The basic copper fractions were determined according to the McLaren and Crawford sequential extraction method. Copper of the solution (intensity) expressed as the equilibrium activity ratio, AR_o^{Cu} when Cu was neither gained nor lost (that is $\Delta Cu_o = 0$) as well as labile Cu (L_{Cu}) was related to the solid soil phase (quantity) considered as the buffering capacity (BC^{Cu}) of the given soils were calculated. The Q/I parameters were estimated at two ionic strengths: 0.005 and 0.010M CaCl_2 . It was found that all parameters depended on the ionic strength and higher values were obtained at 0.010M CaCl_2 . An adverse case occurred for the energy of replacement of calcium by copper (ΔF). Soil properties primarily influenced the magnitude of the Q/I parameters and secondly the high levels of exchangeable and labile soil copper. The low affinity of these soils for copper estimated by the Gapon selectivity coefficients (K_G) supported this assumption.

Keywords: Copper fractions, activity ratio, buffering capacity, contaminated soils

Introduction

Heavy metal accumulation in agricultural soils due to atmospheric fallout or other sources can directly or indirectly affect the quality of land and agricultural products. Plant uptake of heavy metals from soils may cause yield reduction and serious deterioration of its quality with a risk to human health, especially when keeping in mind the long-term persistence of heavy metals in soils even after closure of a plant [10, 20].

Since the early 1970's Poland has been one of the world's leading copper producers. Copper mining and processing has created a serious health hazard to local human populations [19]. Anthropogenic copper in soils is usually characterized by different states of solubility,

which in turn may greatly influence its phytoavailability or general biological toxicity.

A major pool of Cu in relatively less contaminated soils was found to be mostly associated with the residual soil fraction [14, 16], organically bound [8]. The level of exchangeable copper fractions may be very high in some conditions (for example near a copper plant). This fraction considered, as potentially phytoavailable does not provide any detailed information about the activity of the metal in the soil solution. Some attempts aimed at assessing any relationships between copper of the soil solid phase and that in the solution were made [1]. For any cation activity it is convenient to refer to capacity (less available) and intensity (readily available forms). Quantity-intensity (activity) studies have been earlier carried out for elements such as K^+ [3, 21, 27, 29], Mg^{2+} [2], Zn^{2+} [17, 22, 31], Na^+ [13, 24] and also NH_4^+ [4, 28] as well. In the case of copper such reports are scarce presumably

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because Cu is generally present in soils in relatively smaller amounts except areas under anthropogenic pressure. Nevertheless, some reports on copper-calcium thermodynamic evaluation are available [5]. Investigations dealing with some eventual copper toxicity in areas markedly contaminated will be fully carried out with the inclusion of intensity parameters.

The purpose of this work was to investigate i) the distribution of copper fractions in the soils, and ii) the possibility of using Cu-(Ca) exchange isotherm as a simple procedure in soil contamination studies and to point out the usefulness of some exchange parameters for environmental and metal contamination assessment.

Materials and Methods

The investigated soil samples (4) were collected in areas adjacent (*sanitary zone*) to the Glogow Copper Plant in Poland. They were sieved (< 2 mm) and soil particle size was determined areometrically [15] and textural soil classes were established according to Soil Survey Division Staff procedure [25]. Organic carbon was determined by dichromate wet oxidation according to Tiurin, [30] and soil pH in 0.01M CaCl₂ was potentiometrically measured in suspension [23]. Copper fractions as well as iron and manganese oxides were determined according to McLaren and Crawford [16], whereas the cation exchange capacity (CEC) was assessed by a modified Mehlich (pH 8.2) method [12]. Some of these properties are reported in Table 1. Here and after the particular soils will be designated as No. 1, 2, 3 and 4.

Equilibrium and Copper Activity Studies

The equilibrating solutions used for the study were 5×10^{-3} and 1×10^{-2} M Ca(Cl)₂ per liter with different amounts of copper in the range of 1.2×10^{-5} to 4.9×10^{-4} M/L as Cu(Cl)₂. Two grams of appropriate soils and 20 ml of equilibrating solutions (in duplication) shaken for 1 hour and the suspensions were allowed to settle for 24 hours ($t = 25^\circ\text{C}$) preceding filtration. Copper fractions, Fe, Mn as well as equilibrium Cu, Ca and Mg were determined by AAS method (Atomic Absorption Spectrophotometry, Varian Spectra 250 plus). The difference between Cu concentration of the initial (C_o) and equilibrium (C_e) solution represents the amount of Cu gained

($+\Delta\text{Cu}$) or lost ($-\Delta\text{Cu}$) by the soil and is expressed as a quantity factor. The single-ion activities for Cu²⁺ and Ca²⁺ (as a single divalent cation because calcium and magnesium behave similarly in cation exchange reactions) were calculated based on the respective coefficients reported by Tan Kim [26]. Copper activity ratio, designated as AR^{Cu} (intensity factor) was calculated by plotting the latter one against the gain or loss of Cu by the soil ($\pm\Delta\text{Cu}$) on the basis of the procedure reported by Fischer and Niederbudde, [6] adapted for Cu:

$$AR_o^{Cu} = \alpha_{Cu} / \sqrt{\alpha_{Ca}} \quad (1)$$

where:

α_{Ca} and α_{Cu} represent molar activities of Cu²⁺ and Ca²⁺ in the equilibrium solution. The equilibrium activity ratio AR_o^{Cu} when Cu was neither gained nor lost (that is $\Delta\text{Cu}_o = 0$) as well as labile Cu (L_{Cu}) and buffering capacity (BC^{Cu}) were obtained from the plots $\pm\Delta\text{Cu}$ vs AR^{Cu} in their linear portion. The AR_o^{Cu} value, geometrically is the intersection point of the regression line with the abscissa (OX), whereas the labile Cu (L_{Cu}) is the intersection point of the regression with the ordinate (OY). Buffering capacity is obtained from the ratio L_{Cu}/AR_o^{Cu} . The energy of replacement of calcium by copper was calculated on the basis of the equation, as reported by Kotur and Rao, [13].

where:

$$\Delta F = -RT \ln \alpha_{Cu} / \sqrt{\alpha_{Ca}} \quad (2)$$

$$\Delta F = -RT \ln AR_o^{Cu} \quad (3)$$

ΔF - is the free energy of replacement of calcium by copper, (cal K⁻¹ M⁻¹),
 AR_o^{Cu} - represents equilibrium copper activity ratio, (M/L).

Results and Discussion

Soils under threat of contamination generally hold physical and chemical properties that directly or indirectly may qualify these soils for moderate to intensive crop production. The properties of the soils investigated herein are reported in Table 1. It may be observed that acidity seems to be a serious problem since the pH varied slight-

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

Soil type (Number)	pH (0.01M CaCl ₂)	Org. carbon (g kg ⁻¹)	Clay (g kg ⁻¹)	Oxides (mg/kg)		CEC* (cM _e kg ⁻¹)
				Fe	Mn	
Sandy loam (1)	4.65	8.80	255.0	1200.0	162.0	4.51
Sandy loam (2)	4.55	7.80	215.0	1335.0	108.0	3.81
Loamy sand (3)	4.71	9.10	177.0	1550.0	99.0	4.51
Loamy sand (4)	4.65	9.60	231.0	1715.0	227.0	5.36

* Cation exchange capacity

ly and was in the range 4.55 - 4.71. The relative quality of the soils that was roughly estimated by organic carbon (C_{org}) and clay content, as modifiers of the magnitude of the cation exchange capacity (CEC), is relatively low. Organic carbon content did not show any marked variations and was in the limits of 7.80-9.60 g/kg. This relatively low level had a direct influence on the buffering capacities of the soils expressed as CEC, which in turn were comprised within the interval 3.81-5.36 cM_c/kg. These general properties uniformly elucidate the low potential of the soils for intensive agriculture and also their susceptibility to chemical and physical degradation.

Copper Fractions of the Soils

The mentioned properties are not the unique parameters depressing the entire soil quality. Soils of these areas have been threatened for a long time by metals, mainly copper from copper plant activity. The Table 2 reports copper fractions of four soils with different total copper content varying from 17.03 to 44.07 cM_c/kg that is 541.0 to 1400.0 mg/kg, respectively. Within all considered Cu fractions, the organically bound one represented the highest share from 34.0 to 52% of total Cu despite the relatively low organic carbon content of these soils. A share of about 50% or more was earlier pointed out by Grzebisz et al. [8]. Copper is usually found to develop a high affinity to organic substances present in the soil environment. It may be adsorbed either through electro-

tatic bonds (non specific-exchangeable) or by surface complexation (specific adsorption) as reported by Kabata-Pendias and Pendias, [11], Vieira e Silva et al., [31]. The great pool of copper in organic bonds may be an ecological threat, especially for soils poor in organic matter as in the presently studied case. The instability and the release of this organically bound copper fraction may closely be related to soil temperature and additionally to aeration conditions both enhancing the rate of mineralization processes. The exchangeable and weakly bound fractions both quite equally shared in the total Cu content. It was found to be more expressive to report the relative values of their sum, these varying on average from 26 to 35% of total Cu. The markedly high share of these fractions together with that organically bound both directly reflect the real scale of copper contamination, hence a serious threat to be taken into consideration. The water-soluble copper pool directly supports this assumption. The biologically available copper being simultaneously assigned as the threshold value is suggested by Gupta and Haeni [9] to amount to 0.7 mg/kg (i.e. 0.022 cM_c/kg). This level was exceeded several times (from 3 to 9-fold) when referring it to water-soluble copper listed in Table 4. Any increase of calcium (Ca²⁺) ions in the soil solution may consistently lead to an additional release of "active" copper as shown by the relative values of labile Cu in the water-soluble one at 0.0 IOAf CaCl₂, that is from 139.8 to 306.7%. This state incontestably expresses a potential copper toxicity since, as it is well known, the water-soluble copper fraction (commonly labile copper)

Table 2. Copper fractions determined according to McLaren and Crawford (1973), (cM_c kg⁻¹).

Soil	Cu-H ₂ O	Cu-CaCl ₂	Cu-AAc	Cu-K ₄ P ₂ O ₇	Cu-Ox 3.25	Cu-Res (HF)	Sum
Sandy loam (1)	0.082	2.34	2.70	6.90	4.18	0.82	17.03
Sandy loam (2)	0.066	2.54	3.21	7.62	7.64	1.02	22.10
Loamy sand (3)	0.198	5.91	5.29	16.86	2.48	1.59	32.33
Loamy sand (4)	0.132	6.08	6.96	19.83	7.18	3.88	44.07
<i>Cu forms</i>	<i>Water soluble</i>	<i>Exchangeable</i>	<i>Mineral</i>	<i>Organically bound</i>	<i>Occluded</i>	<i>Residual</i>	

Table 3. Copper quantity-intensity parameters and free energy of replacement of calcium by copper.

Soil	Ca(Cl) ₂ (M/L)	Cu labile (L _{Cu}) (cM _c kg ⁻¹)	AR _o ^{Cu(1)} (ML ⁻¹)	BC ^{Cu(2)} (cM _c kg ⁻¹ /M L ⁻¹)	ΔF ⁽³⁾ (cal M ⁻¹ K ⁻¹)	K _G ⁽⁴⁾ (L M ⁻¹)
Sandy loam (1)	0.005	-0.048	0.044	1.09	1849	0.24
	0.010	-0.115	0.063	1.83	1637	0.41
Sandy loam (2)	0.005	-0.083	0.071	1.16	1566	0.30
	0.010	-0.161	0.096	1.68	1387	0.44
Loamy sand (3)	0.005	-0.134	0.107	1.22	1323	0.27
	0.010	-0.358	0.118	3.03	1265	0.67
Loamy sand (4)	0.005	-0.166	0.108	1.52	1318	0.28
	0.010	-0.405	0.109	3.72	1312	0.69

⁽¹⁾ Equilibrium activity ratio, ⁽²⁾ Buffering capacity for Cu, ⁽³⁾ Energy of replacement of calcium by copper, ⁽⁴⁾ Relative affinity for Cu ($K_G = BC^{Cu}/CEC$).

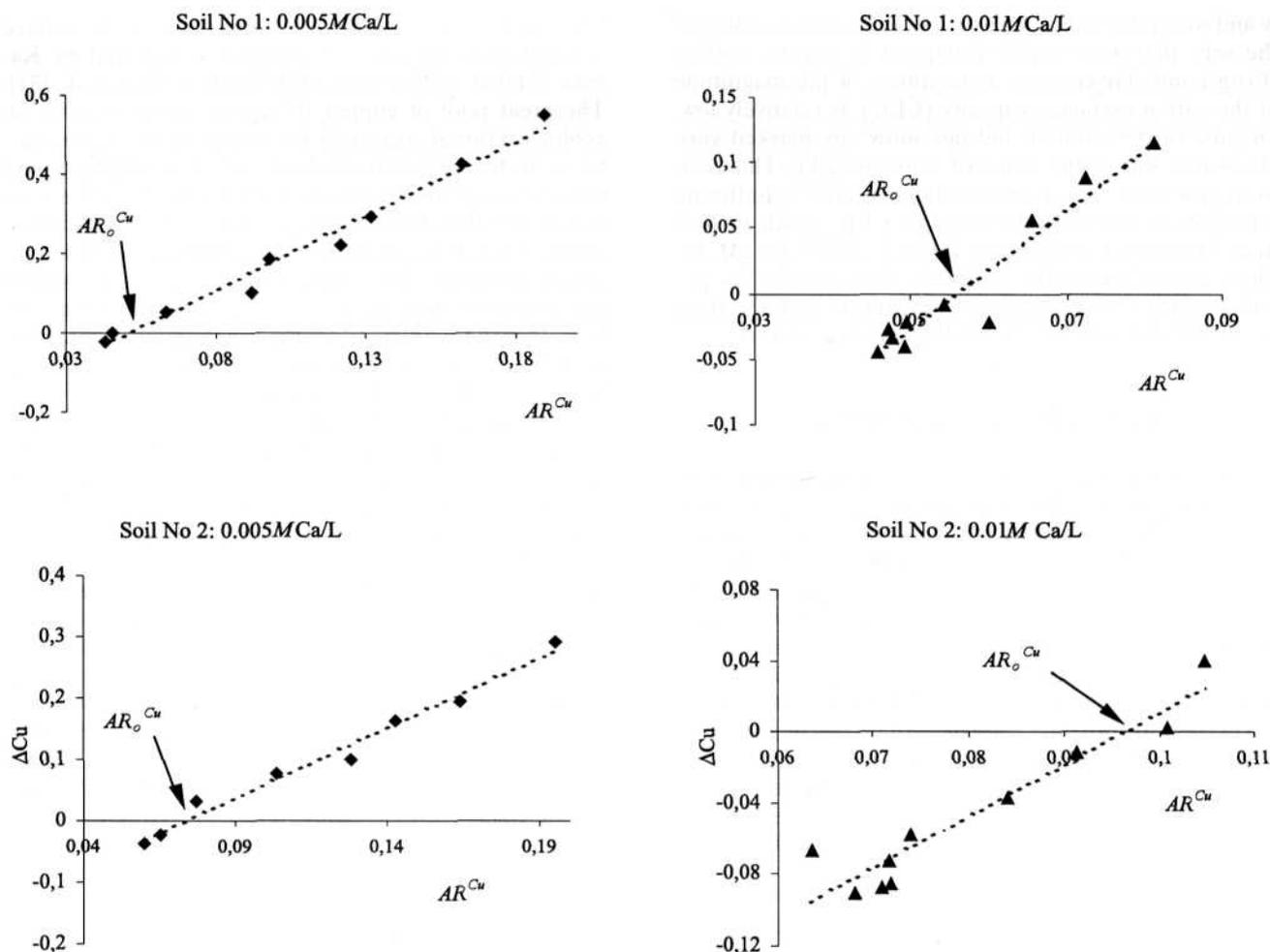


Fig. 1. The effect of calcium concentration on copper equilibrium activity ratio, AR^{Cu} of soils No. 1 and No. 2.

may be directly assimilated by microorganisms and plants. The behaviour of copper in the soil is undoubtedly dependent on soil pH [18] and the type of calcium used. Acidic soils are neutralized by the application of alkalinizing materials such as CaO, CaCO₃ or others. In similar conditions the "active" soil copper as well as calcium may behave differently in comparison to the calcium type herein applied. These assumptions are greatly over the scope of this paper.

Quantity-Intensity Relationship

The use of quantity-intensity approach for assessing exchange reactions of highly contaminated soils is complex. There is no fully satisfactory reason for assuming that copper toxicity or bioavailability depends only on its "concentration" in the soil solution. The important quantity of soluble copper may be examined in terms of ion activity. Table 3 sums up the quantity-intensity parameters of the soils equilibrated at two ionic strengths (0.005 and 0.01M CaCl₂). All the calculated values depended closely on the equilibrating medium: the higher the calcium concentration of the solution the highest the

appropriate copper exchange parameters, with exception for the free energy of replacement of calcium by copper. The Q/I curves in the various soils are shown in Figures 1 and 2. As it could be observed in all these soils the curves lack the lower curved part that is observed in typical Q/I curve, irrespective of the calcium background. The lack of curvature can be assigned to two possible reasons:

1) the soils may lack specific exchange sites which can hold copper more strongly,

2) the soils may contain a large amount of exchangeable copper such that the effect would not be noticed. These two points were widely outlined by the great level of the loosely bound copper fractions reported earlier in Table 2. Such a behaviour could be expected since the buffering properties of all soils were sensitively low. The share of copper in the cation exchange capacity expressed as the buffering capacity (BC^{Cu}) was in the average of 30% for the lower calcium ionic strength (0.005M CaCl₂), but varied from 41 to 69% in the case of the higher ionic medium.

In terms of direct metal impact on the soil environment it seems more useful and practical to manage the labile copper pool (Lc_u) and the appropriate Cu²⁺ equi-

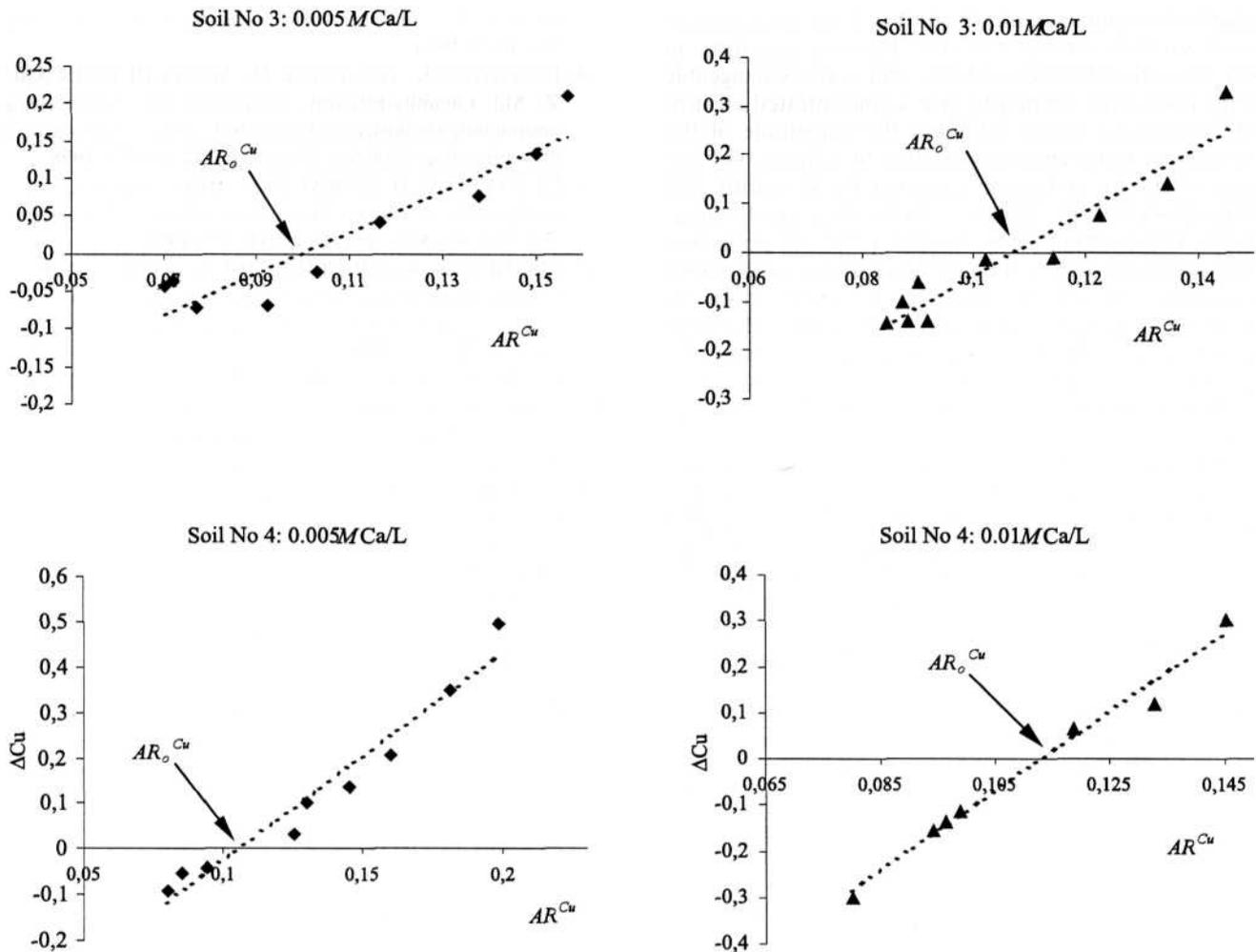


Fig. 2. The effect of calcium concentration on copper equilibrium activity ratio, AR_o^{Cu} of soils No. 3 and No. 4

librium activity (AR_o^{Cu}) in the soil solution. Both parameters were obtained from the Q/I system. The first one is a mean of the amount of copper that is potentially phytoavailable (bioavailable). The labile Cu pool changed accordingly to the concentration of Ca in the equilibrating solution and varied from 0.048 cM_c/kg (1.52 mg/kg) to 0.166 cM_c/kg (5.28 mg/kg) for the 0.005M $CaCl_2$ concentration, irrespective of the soils. A range of 0.115 cM_c/kg (3.64 mg/kg) to 0.405 cM_c/kg (12.87 mg/kg) was found for the respective soils at 0.010M $CaCl_2$. This pool may be potentially subject to leaching processes in conditions similar to these herein presented and additionally as listed in Table 4 mainly for the high share of L_{Cu} in the water-soluble fraction. The relative activity of copper (Cu^{2+}) to calcium (Ca^{2+}) ions at the equilibrium state was expressed by their ratio AR_o^{Cu} . The higher the AR_o^{Cu} values the bigger the Cu pool in the equilibrating solution, the probable copper toxicity occurrence. It is worth mentioning that ionic strength also influenced the magnitude of the equilibrium activity ratio similarly as in the case of L_{Cu} .

The energy of replacement (AF) of calcium by copper was found to be related both to the level of copper of the soils and to the equilibrating medium. The higher the

Table 4. Percentage share of the labile Cu pool in water soluble and exchangeable copper fractions determined according to McLaren and Crawford [16] at two calcium chloride levels.

Soil	Cu-labile in			
	Cu – water soluble		Cu – exchangeable	
	0.005ML ⁻¹ *	0.01ML ⁻¹	0.005ML ⁻¹	0.01ML ⁻¹
(%)				
Sandy loam (1)	58.8	139.8	2.3	5.2
Sandy loam (2)	125.5	244.1	3.3	6.5
Loamy sand (3)	67.7	180.5	2.4	6.3
Loamy sand (4)	125.9	306.7	2.8	6.8

* M $Ca(Cl)_2$ L⁻¹

total Cu level the lowest the replacement energy values, irrespective of the equilibrating medium. The decrease of AF values with increasing the ionic strength from 0.005 to 0.010M $CaCl_2$ was similar for soils No. 1 and 2 (11%), soil No. 3 (5%) and about 0.4% for soil No. 4. According to Woodruff [32] a dilute electrolyte may be viewed as an

excellent instrument with which to evaluate the energetics of cationic exchange for soils. This was unrealistic in our case since the level of labile and even exchangeable copper was high enough to give a concentrated electrolyte that could greatly influence the magnitude of the energies of replacement of calcium by copper. The energy values for potassium reported by Woodruff [32] ranged widely from - 2000 to - 4000 calories/mol, whereas the values obtained by Terelak [27] with potassium changes in soil were in the interval of 1800 to about 3000 calories/mol. We obtained relatively low values which depended closely on the ionic strength and the soil copper level (Table 3). Then the weaker the ionic strength the highest the ΔF values and the higher the soil Cu content the lowest the energy of replacement of calcium by copper.

The relative affinity of the soils for copper was also estimated by the use of the Gapon selectivity coefficient $K_G = BC^{Cu}/CEC$, after Thompson and Blackmer, [28] and Egashira et al., [4]. The calculated values were relatively low and varied less for 0.005M $CaCl_2$ (between 0.24 and 0.28 $L M^{-1}$) than for 0.010M $CaCl_2$ (0.41 - 0.69 $L M^{-1}$). Such a low affinity of copper to the soil solid phase could be expected and be attributed both to the low organic matter content and additionally to the weak buffering capacities (CEC) of all the soils. Another explanation of this state could be a high saturation of most of active sorption sites as a consequence of the great anthropogenic copper input. The high labile and exchangeable copper level of the soils supports this assumption.

Conclusions

1. Investigated soils were acidic and additionally characterized by markedly low organic matter content and cation exchange capacity.
2. Copper in organic bonds was found to represent the highest copper pool among other fractions. This share varied from 34 to 52% of total copper for all soils.
3. Equilibrium activity ratio (AR_o^{Cu}), buffering capacity (BC^{Cu}), labile copper (Lc_u) were related both to the levels of soil copper and the ionic strength of the equilibrating solution. Lower values were obtained at 0.005M and higher at 0.010 M $CaCl_2$.
4. Copper affinity (K_G) to the soils was relatively low. This could be attributed to the low organic matter content and buffering capacities and to the high levels of total soil copper as well.
5. The energy of replacement of calcium by copper (ΔF) varied in relatively short limits between the lowest and the highest ionic strength. The higher the total soil copper level the lowest the AF values.

References

1. ABD-ELFATTAH A., WADA KOJI. Adsorption of lead, copper, zinc, cobalt, and cadmium by soils that differ in cation-exchange materials. *Jour. Soil Sci.*, **32**, 271, **1981**.
2. ALSTON A. M. Availability of magnesium in soils. *J. Agric. Sci.* **70**, 197, **1972**.
3. BECKETT P. H. T. Studies on soil potassium. II. The intermediate Q/I relation of labile potassium in the soil. *J. Soil Sci.* **15**, 9, **1964**.
4. EGASHIRA K., HAGIMINE M., MOSLEHUDDIN ABU Z. Md. Quantity-Intensity relationship for characterizing ammonium chemistry of Bangladesh soils in reference to clay mineralogy. *Soil Sci. Plant Nutr.*, **44** (3) 377, **1998**.
5. EL-SAYED M. H., BURAU R. G., BABCOCK K. L. Thermodynamics of copper (II)-calcium exchange on bentonite clay. *Soil Sci. Soc. Amr. Proa*, **34**, 397, **1970**.
6. FISCHER W. R., NIEDERBUDDER E. A. Die exakte und schnelle Bestimmung von K/Ca Austauschkurven an Boden und die Automatisierung ihrer Auswertung. *Landwirtsch. Forsch.*, **32**, 207, **1979**.
7. GRZEBISZ W., KOCIALKOWSKI W. Z. Evaluation of simple soil tests for quantitative assessment of copper fractions in polluted soils. *Pollutants in Environment*, 3, 66 (in Polish with English summary), **1993**.
8. GRZEBISZ W., KOCIALKOWSKI W. Z., CHUDZINSKI B. Copper geochemistry and availability in cultivated soils contaminated by a copper smelter. *Jour. Geoch. Exploration* **58**, 310, **1997**.
9. GUPTA S. K., HANI H. Methode pour determiner dans les sols les concentrations des metaux lourds disponibles pour les plantes et les microorganismes et verification dans les regions contaminees. *FAC Liebefeld, Nr 2. Bern*, **1989**.
10. HUTCHINSON T., SHAGER S. Recovery and persistence of metal stress in a forested ecosystem near Sudbary, Ontario 66 years after closure of the O'Donnell roast bed. *Proceed, of the Symposium Heavy metals in the Environment, Hamburg*, **1995**.
11. KABATA-PENDIAS A. Behavioural properties of trace metals in soils. *Applied Geochemistry, Suppl. Issue 2*, pp 3, **1993**.
12. KOCIALKOWSKI W. Z., RATAJCZAK M. J. A simplified method for exchangeable cations and cation exchange capacity determination in soil according to Mehlich. *Rocz. AR-Poznan; CXLVI*, 106 (in Polish), **1984**.
13. KOTUR S. C., SESHAGIRI RAO T. Quantity/intensity and quality potential studies in Na/Ca exchange system in some salt-affected soils. *Jour. Soil Sci.*, **39**, 199, **1988**.
14. LEVESQUE M. P., MATHUR S. P. Soil tests for copper, iron, and zinc in histosols. The influence of soil properties, iron, manganese and zinc on the level and distribution of copper. *Soil Sci. Soc. Am. J.*, **42**, 421, **1986**.
15. LITYNSKI T., JURKOWSKA H., GORLACH E. *Analiza chemiczna*. PWN, Warszawa, **1976**.
16. MCLAREN R. G., CRAWFORD D. V. Studies on soil copper. I. The fractionation of copper in soils. *Journal of Soil Science*, **24**, 172, **1973**.
17. MESQUITA M. E., VIEIRA E SILVA J. M. Zinc adsorption by calcareous soil. Copper interaction. *Geoderma* **69**, 137, **1996**.
18. MSAKY J. J., CALVET R. Adsorption of copper and zinc in soils, influence of pH on adsorption characteristics. *Soil Science*, **150** (2), 513, **1990**.
19. NIETUPSKI T. An assessment of farm losses of crop yields due to emissions from the Glogow Copper Smelter Report, 13 pp., *Agricul. Univer. in Wroclaw*, **1994**.
20. NRIAGU J.O. Global metal pollution. *Environment*, **32** (7), 7, **1990**.
21. PASRICHA N. S. Potassium Q/I relationships as influenced by calcium and magnesium treated as separate ionic species, and by soil submergence. *J. Agric. Sci.* **104**, 577, **1985**.

22. PASRICHA N. S, BADDESHA H. S, M. S. AULAKH, NAYYAR V. K. The Zn quantity-intensity relationships in four different soils as influenced by phosphorus. *Soil Sci.* **143** (1), **1**, **1987**.
23. Polska Norma, Polski Komitet Normalizacyjny, nr ref. PrPN-ISO 10390 (E), Jakość gleby i oznaczanie pH. Pierwsze wydanie **1994**.
24. RIEU M., TOUMA J., GHEYI H. R. Sodium-calcium exchange on Brazilian soils, modeling the variation of selectivity coefficients. *Soil Sci. Soc. Am. J.*, **55**, 1294, **1991**.
25. Soil Survey Division Staff, *Soil Survey Manual*. USDA, Handbook Np. 18, **1993**.
26. TAN KIM H. *Principles of soil chemistry*. Second Edition, Marcel Dekker, Inc., **1993**.
27. TERELAK H. Wpływ nawożenia potasem na kształtowanie się statycznych i dynamicznych wskaźników zawartości tego pierwiastka w glebie. *Roczniki Gleboznawcze*, Warszawa T. XXX, **3**, 157, **1979**.
28. THOMPSON T. L., BLACKMER A. M. Quantity-Intensity relationships of soil ammonia in long-term rotation plots. *Soil Sci. Soc. Am. J.* **56**, 494, **1992**.
29. TINKER P. B. Studies on soil potassium. **III**. Cation activity ratios in acid Nigerian soils. *Jour. Soil Sci.*, **15** (1), 24, **1964**.
30. TIURIN N. W. K metodické analíza dla sprawnitélného izučeníja sostawa počwienného pieregnoja ili gumusa. Rabota po organiczeskomu wieszczestwu počwzy. Moskwa, **1951**.
31. VIEIRA E SILVA J. M., DOMINGUES H., MESQUITA M. E. Sequential fractionation of copper and zinc from sewage sludges. Use of organic solvents. *Int. J. Environ. Anal. Chem.* **51**, 109, **1993**.
32. WOODRUFF C. M. The energies of replacement of calcium by potassium in soils. *Soil Sci. Soc. Proc.* **19**, 167, **1955**.