J. Elementol. 2009, 14(1): 55-62

SOLUBLE FORMS OF ZINC IN PROFILES OF SELECTED TYPES OF ARABLE SOILS

Jolanta Domańska

Department of Agricultural and Environmental Chemistry
University of Life Sciences in Lublin

Abstract

The research was carried out on arable soils of the region of Lublin. The aim of the study was to determine the content of Zn extractable in 1 M $HCl \cdot dm^{-3}$ in profiles of selected types of soils and the total content of Zn (measured in aqua regia) in soil samples from the accumulative layer 0-20 cm of the soils. The investigations included 8 morphological types of soils: Rendzic Leptosols (typical rendzinas), Rendzic Leptosols (humic rendzinas), Haplic Phaeozems, Calcaric Cambisols, Haplic Luvisols, Cambic Arenosols, Haplic Podzols, Eutri-Terric Histosols. The content of zinc (Zn) was measured by Atomic Absorption Spectrometry (AAS). In mineral soils the highest content of total Zn was found in rendzinas (48.0-55.8 $mg \cdot kg^{-1}$ DM) and the lowest one appeared in rusty soil and in podzolic soil – about 13 mg $Zn \cdot kg^{-1}$ each, at average 24.5 $mg \cdot kg^{-1}$. Average concentration of available forms of zinc was 5.2 mg $Zn \cdot kg^{-1}$. The amount of this element in soils was from 2.0 mg $Zn \cdot kg^{-1}$ in the level Cca of typical rendzinas to 17.0 mg $Zn \cdot kg^{-1}$ in the accumulative level of peat soil. In most profiles the highest concentration of soluble form of Zn was present in the accumulative layer and was usually decreasing deeper in the profile. The distribution of Zn in profiles was shaped by the biological accumulation of this element in the humus horizon and natural biogeochemical processes.

Key words: zinc, total contents, available forms, rendzina, chernozem soil, brown soil, lessive, rusty soil, podzolic soil, peat soil.

dr Jolanta Domańska, Department of Agricultural and Environmental Chemistry, University of Life Sciences, ul. Akademicka 15, 20-950 Lublin, Poland, e-mail: jolanta.domanska@up.lublin.pl

ROZPUSZCZALNE FORMY CYNKU W PROFILACH WYBRANYCH TYPÓW GLEB UŻYTKOWANYCH ROLNICZO

Abstrakt

Badania przeprowadzono na glebach użytków rolnych Lubelszczyzny. Celem badań było określenie zawartości cynku przyswajalnego (po ekstrakcji próbek 1 mol $HCl \cdot dm^{-3}$) w profilach wybranych typów gleb oraz jego zawartości ogólnej w próbkach z poziomu akumulacyjnego 0-20 cm (po ekstrakcji w wodzie królewskiej). Badaniami objęto 8 typów gleb, takich jak: rędzina właściwa, rędzina czarnoziemna, czarnoziem zdegradowany, gleba brunatna, gleba płowa, gleba rdzawa właściwa, gleba bielicowa właściwa oraz gleba torfowa. Stężenie cynku w przesączach glebowych oznaczono za pomocą spektrofotometru absorpcji atomowej (ASA). W glebach mineralnych najwyższą zawartość Zn ogółem stwierdzono w rędzinach (48,0-55,8 $mg \cdot kg^{-1}$ s.m.), najniższą zaś w glebie rdzawej i bielicowej – ok. 13 mg $Zn \cdot kg^{-1}$, średnio 24,5 $mg \cdot kg^{-1}$. Średnia zawartość cynku przyswajalnego wynosiła 5,2 mg $Zn \cdot kg^{-1}$. Zawartość tego składnika wahała się od 2,0 mg $Zn \cdot kg^{-1}$ w poziomie Cca rędziny właściwej do 17,0 mg $Zn \cdot kg^{-1}$ w poziomie akumulacyjnym gleby torfowej. W większości profili zawartość rozpuszczalnej formy Zn jest na ogół zdecydowanie wyższa w poziomie orno-próchnicznym i maleje wraz z głębokością. Takie rozmieszczenie cynku w profilach zostało spowodowane głównie akumulacją biologiczną w poziomie próchnicznym oraz naturalnymi procesami biogeochemicznymi.

Słowa kluczowe: cynk, zawartość ogólna, formy przyswajalne, rędzina, czarnoziem, gleba brunatna, gleba płowa, gleba rdzawa, gleba bielicowa, gleba torfowa.

INTRODUCTION

Zinc is a natural component of soils, and its content depends primarily on the type of mother rocks and soil-forming processes. In agricultural areas, zinc excess originates mainly from man-made sources (industry, transport, waste substances, plant protection chemicals), which contribute to increased zinc concentration, mainly in the accumulative soil layer. Studies on the total content and the amount of available forms of microelements, including zinc, in the surface soil layer, have been carried out for many years. However, fewer smaller publications deal with concentration of available forms of microelements in deeper layers of the soil profile. Zinc occurs in soils as easily soluble compounds, which favors its migration, especially when the soil is acidic in reaction (Terelak et al. 2000, Van Oort et al. 2006). I t an be expected that mobile forms of zinc, which determine its availability to plants, will appear in different amounts in particular genetic horizons of soils belonging to different types. Determination of zinc not only in the arable layer but also in deeper horizons of a profile enables us to evaluate the abundance of zinc and to predict, more precisely, its deficiency or excess to crops.

The present study was completed in order to evaluate and assess total zinc content and zinc available forms profiles of several types of arable soils in the Lublin region.

MATERIAL AND METHODS

Examinations were carried out in October 2003 in the Lublin region. The study material consisted of the following soil morphological types: Rendzic Leptosol developed from calcaric rock, Rendzic Chernozem, Haplic Phaeozem, Calcaric Cambisol developed from loess, Haplic Luvisol developed from dust, Cambic Arenosol, Haplic Podzol developed from loamy sand, and Eutri-Terric Histosol. Two to five samples were collected from each soil type and particular horizons. Selected profiles are represented by arable soils (profiles No 1-7) and durably sodded soils (profile No 8). These profiles (No 1-8) were present in the following sites: Guzówka (No 1), Żdanówek (No 2), Rogów (No 3), Tarnawa (No 4), Łosień (No 5), Kąty (No 6), Wólka Orłowska (Nos 7 and 8).

The soil samples were air-dried, then ground in a porcelain mortar and passed through a 1 mm mesh sieve. The following properties were then determined: granulometric composition with Casagrande's areometric method as modified by Prószyński, pH by potentiometry in 1 mol $KCl \cdot dm^{-3}$, hydrolytical acidity (Hh) with Kappen's method, total carbon content with Tiurin's method. Concentrations of soluble zinc forms were determined by AAS after extraction with 1 $mol \cdot dm^{-3}$ hydrochloric acid solution (Rinkis's method). The total zinc content was analyzed after dissolving each sample in aqua regia composed of acids mixed at a 3:1 proportion, according to the Polish norm PN-ISO 11466. Zinc concentrations in soil filtrates were determined by means of the AAS flame technique. Zinc solubility was expressed as a percentage of zinc forms extracted with HCl solution in the total zinc content.

RESULTS AND DISCUSSION

Basic physicochemical properties of the soil are presented in Table 1, while the data related to the total zinc content and its forms extractable in 1 mol $HCl \cdot dm^{-3}$ can be found in Table 2.

The analysis of total zinc revealed that the soil types chosen for the study were not abundant in this element. In the accumulative soil layer (0-20 cm), the total Zn concentration varied from 13.2 to 55.8 $mg \cdot kg^{-1}$ of soil DM, with the mean level of 24.5 mg $Zn \cdot kg^{-1}$. Typical rendzina (Rendzic Leptosols) and humic rendzina (Rendzic Leptosols) were characterized by the highest zinc contents (55.8 $mg \cdot kg^{-1}$ and 48.0 $mg \cdot kg^{-1}$, respectively). Lower zinc levels were found in Chernozem, Cambisol, and Luvisol soils: 39.5; 37.8, and 27.2 $mg \cdot kg^{-1}$, and the lowest concentration of zinc (about 13 $mg \cdot kg^{-1}$) occurred in soils of light and very light granulometric composi-

Table 1

Physicochemical properties of soils

Profile No	Type	Horizon	Depth (cm)	pH_{KCl}	Hh (mmol) $(+)\cdot kg^{-1}$)	Org. C ($g\cdot kg^{-1}$)	(%) fraction of diameter (mm)		
							0.1-0.02	0.02-0.002	<0.002
1	Rendzic Leptosols (typical rendzinas)	Apca Cca	0-27 < 27	6.84 7.08	3.75 1.50	17.6 7.4	27 30	33 14	26 15
2	Rendzic Leptosols (humic rendzinas)	Apca Apca Cca	0-30 30-55 < 55	6.94 7.07 7.13	4.50 3.00 2.25	24.25 8.26 11.61	16 16 15	21 34	18 32 32
3	Haplic Phaeozems (chernozem)	Ap Ah AhBbr BbrC Cca	0-20 20-42 42-60 60-90 < 90	6.69 6.95 6.25 7.29 7.31	9.00 4.50 0.75 0.75 0.70	17.54 14.19 6.97 6.19 3.87	57 58 59 59 59	30 30 27 27 28	7 8 12 12 11
4	Calcaric Cambisols (brown soil)	Ap Bbr BbrC C	0-24 24-65 65-110 < 110 < 140	4.32 4.53 4.98 5.33 7.00	43.50 23.25 15.00 10.50 3.00	11.61 4.13 3.10 2.32 4.13	50 49 46 61 56	30 28 27 25 37	15 19 16 12 4
5	Haplic Luvisols (lessive)	ApEet Eet (AEt) Bt BtR	0-24 24-40 40-70 70-95	6.27 6.05 5.80 3.80 -	8.25 7.50 7.50 37.50 -	11.09 4.13 3.61 2.84	50 49 45 28 -	33 33 27 23 -	7 10 22 29 -
6	Cambic Arenosols (rusty soil)	Ap Bv C	0-30 30-80 < 80	4.60 3.68 3.80	23.25 13.50 6.00	14.70 4.64 2.32	28 5 1	7 0	2 3 0
7	Haplic Podzols (podzolic soil)	Ap Ees Bfe C	0-30 30-50 50-85 < 85	6.44 5.14 5.48 5.76	7.13 4.50 10.50 8.25	9.68 1.55 1.81 0.90	42 49 25 17	10 11 31 0	3 4 12 5
8	Eutri-Terric Histosols (peat soil)		0-22 22-32 <32	6.34 5.93 5.66	12.00 12.01 12.75		peat	peat	peat

Table 2

The content and solubility of zinc in soils

Profile No	Type	Horizon	Zn total ($mg \cdot kg^{-1}$)	Zn in 1M $HCl \cdot dm^{-3}$ ($mg \cdot kg^{-1}$)	Solubility of Zn (%)*
1	Rendzic Leptosols (typical rendzinas)	Apca Cca	55.8 -	8.4 2.0	15.0 -
2	Rendzic Leptosols (humic rendzinas)	Apca Apca Cca	48.0 - -	6.7 3.2 2.8	14.0 - -
3	Haplic Phaeozems (chernozem)	Ap Ah AhBbr BbrC Cca	39.5 - - - -	9.6 5.2 4.8 4.9 4.5	24.3 - - - -
4	Calcaric Cambisols (brown soil)	Ap Bbr BbrC C	37.8 - - - -	5.7 3.0 4.6 3.5 6.6	15.1 - - - -
5	Haplic Luvisols (lessive)	ApEet Eet (AEt) Bt BtR	27.2 - - - -	5.7 3.1 3.9 3.5 -	21.0 - - - -
6	Cambic Arenosols (rusty soil)	Ap Bv C	13.2 - -	4.2 5.5 2.6	31.9 - -
7	Haplic Podzols (podzolic soil)	Ap Ees Bfe C	13.7 - - -	6.9 2.3 3.1 3.2	50.4 - - -
8	Eutri-Terric Histosols (peat soil)	Mt O_1tni O_2tni	- - -	17.0 8.3 4.6	- - -
Mean			24.5	5.2	-

*percentage of soluble forms in total content of metal

tion, i.e. Arenosol and Podzolic soils. The analysis of the experimental data indicates that the highest zinc amount was present in soils characterized by a high humus content and large amounts of finest particles. According to TERELAK et al. (2000), zinc content in soil depends on a soil type, and is strongly conditioned by the soil's granulometric composition. In acidic brown soils, SKŁODOWSKI and ZARZYCKA (1997) determined about 35 mg $Zn \cdot kg^{-1}$ in the humus horizon, and that concentration decreased deeper in the profile. These authors claimed that zinc accumulation in the humus layer is a product of biological accumulation of this element and agricultural use of the soil. Different sub-types of gypsum rendzinas examined by NIEMYSKA-ŁUKASZUK and CIARKOWSKA (1999) were characterized by the highest total zinc concentrations in surface layers, which tended to decrease in deeper layers of the profile. These authors found statistically significant dependence of total zinc on colloid clay content. Also TERELAK et al. (2000) confirmed significant correlation between zinc amounts in soils and such properties as < 0.02 mm fraction content, organic matter content, and pH, which indicates, in the authors' opinion, that zinc presence in soils also depends on other factors.

Total zinc content in the 0-20 cm layer of the soils we examined did not exceed values accepted as the natural background in evaluation of soil contamination, which is 50 $mg \cdot kg^{-1}$ for very light and light soils, and 100 $mg \cdot kg^{-1}$ for heavy soils (KABATA-PENDIAS et al. 1993).

Concentration of zinc extractable in 1 mol $HCl \cdot dm^{-3}$ varied between particular soil profiles. In most of the profiles, this form appeared in higher amounts in the humus horizon, where it reached the levels from 4.2 to 17.0 $mg \cdot kg^{-1}$, than in deeper layers. Brown soil was an exception (profile No 4), as it contained 6.6 mg $Zn \cdot kg^{-1}$ in the mother rock horizon, hence more Zn than within surface layer Ap (5.7 $mg \cdot kg^{-1}$). Another exception was Arenosol, containing slightly more zinc in Bv (5.5 $mg \cdot kg^{-1}$) than in Ap horizon (4.2 $mg \cdot kg^{-1}$). The content of the zinc form examined in 5 soil types (Rendzic Leptosol, Rendzic Chernozem, Haplic Phaeozem, Cambic Arenosol, and Eutri-Terric Histosol) apparently decreased with the profile depth. Such a tendency did not occur in Cambisol and Luvisol soils. However, large differentiation in the content of zinc in particular horizons confirmed the influence of elution processes on the distribution of this element within a profile. VAN OORT et al. (2006), when examining the dynamics of Zn behavior, observed that the metal was moved in soil mainly in a dissolved form, unlike Pb which moved mainly in a colloidal form. The authors also found that the interaction of the soil solution and specific pedological features leads to enhanced Zn accumulation in clay-iron coatings characteristic of illuvial B horizon. BARAN et al. (2003) reported that it was only the genetic horizon that affected the content of zinc extractable in 1 mol $HCl \cdot dm^{-3}$ in Podzolic soils. According to these authors, higher concentrations of this form of zinc, like total zinc content, occurred in the humus horizon rather than in deeper layers. KORZENIOWSKA and STANISŁAWSKA-GLUBIAK (2004) determined a high correlation coefficient between organic matter and zinc extractable in 1 mol $HCl \cdot dm^{-3}$, although they did not achieve significant correlations between organic matter and zinc amounts in plants. Also GAMBUŚ et al. (2004) did not find strong correlations between Zn concentration in plants and Zn extracted from the soil using 1 mol $HCl \cdot dm^{-3}$, except for oats roots. However, these authors recorded a very strong correlation between zinc content in plants and the metal level extracted with non-buffered solutions with low extraction strength. On the basis of our results regarding available zinc forms in the examined mineral soil types from the Lublin region, it can be stated that profiles Nos 1-5, characterized by the granulometric composition of heavy soil, showed low zinc abundance, while very light and light soils (profiles Nos 6 and 7) revealed high abundance (ZALECENIEA NAWOZOWE 1990).

Zinc solubility in rendzinas and Calcaric Cambisol was poor (14-15%), while higher solubility was recorded in Luvisol (21%) and Haplic Phaeozem (24%); the best zinc solubility was observed in Arenosol and podzolic soils (32% and 50%, respectively). BADORA (2002) reported that binding of heavy metals ions by organic matter depended on the soil acidity. Zinc at pH 5.8 is bound by humic acids up to 60% of its cationic concentration, whereas at lower pH values, its sorption almost disappears. This may explain low Zn solubility in the rendzinas and high one in Arenosol and podzolic soils. Furthermore, a relatively large percentage of soluble forms in the total zinc content in light soils may indicate that Zn was supplied from anthropogenic sources. According to TERELAK et al. (2000), zinc migration within the environment is favored by low acidity of soil as well as humus substances, namely fulvic acids and some fractions of humic acids forming soluble complexes.

CONCLUSIONS

1. The mean content of available zinc (extractable with 1 mol $HCl\cdot dm^{-3}$) in the soils was 5.15 $mg\cdot kg^{-1}$ DM. In most of the soils examined, except Cambisol and Arenosol, the highest amounts of available zinc were present in the humus horizon, decreasing deeper in a soil profile depth.

2. Cambisol and luvisol soils were characterized by high abundance in zinc extractable in 1 mol $HCl\cdot dm^{-3}$, while rendzinas and Chernozem by were low in this form of zinc; the highest zinc concentration was recorded in Eutri-Terric soil.

3. The zinc solubility in studied soils can be put in the following order: Rendzic Chernozem < Rendzic Leptosol = Calcaric Cambisol < Haplic Luvisol < Haplic Phaeozem < Cambis Arenosol < Haplic Podzol.

REFERENCES

BADORA A. 2002. *Wpływ pH na mobilność pierwiastków w glebach.* Zesz. Probl. Post. Nauk Rol., 482: 21-36.

BARAN S., WÓJCIKOWSKA-KAPUSTA A., GOSTKOWSKA K. 2003. *Zmiany zawartości miedzi i cynku w glebach odłogowanych.* Zesz. Probl. Post. Nauk Rol., 493, 305-310.

GAMBUŚ F., RAK M., WIECZOREK J. 2004. *Wpływ niektórych właściwości gleby na fitoprzyswajalność i rozpuszczalność cynku, miedzi i niklu w glebie.* Zesz. Probl. Post. Nauk Rol., 502: 71-79.

KABATA-PENDIAS A., MOTOWICKA-TERELAK T., PIOTROWSKA M., TERELAK H., WITEK T. 1993. *Ocena stopnia zanieczyszczenia gleb i roślin metalami ciężkimi i siarką.* P(53), IUNG – Puławy, 1-20.

KORZENIOWSKA J., STANISŁAWSKA-GLUBIAK E. 2004. *Wpływ materii organicznej na dostępność cynku i pozostałych mikroelementów dla roślin pszenicy*. Zesz. Probl. Post. Nauk Rol., 502: 157-164.

NIEMYSKA-ŁUKASZUK J., CIARKOWSKA K. 1999. *Zawartość cynku, ołowiu i kadmu w profilach różnych podtypów rędzin gipsowych*. Zesz. Probl. Post. Nauk Rol., 467: 439-447.

VAN OORT F, JONGMANS A. G. CITEAU L. LAMY I. CHEVALLIER P. 2006. *Microscale Zn and Pb distribution patterns in subsurface soil horizons: an indication for metal transport dynamics*. Europ. Soil Sci., 57 (2): 154-166.

SKŁODOWSKI P., ZARZYCKA H. 1997. *Wpływ użytkowania gleb na zawartość i rozmieszczenie metali ciężkich*. Roczn. Glebozn., 48: 5-13.

TERELAK H., PIETRUCH C., TUJAKA A. 2000. *Występowanie cynku w poziomach powierzchniowych gleb użytków rolnych Polski*. Zesz. Probl. Post. Nauk Rol., 472: 645-651.

Zalecenia Nawozowe 1990. *Liczby graniczne do wyceny zawartości w glebach makro- i mikroelementów*. Cz. I., IUNG, Puławy, (P) 44-26.