J. Elem. s. 7–15

DOI: 10.5601/jelem.2014.19.1.610

ORIGINAL PAPERS

THE PROFILE DISTRIBUTION OF ZINC IN ARABLE ALLUVIAL SOILS WITH NATURALLY ELEVATED CONTENT OF CALCIUM CARBONATE

Agata Bartkowiak[1], Jacek Długosz[1], Ryszard Zamorski[2]

[1]Chair of Soil Science and Soil Protection[1]
[2]Department of Biochemistry
University of Technology and Life Sciences in Bydgoszcz

Abstract

The objective of the study was to analyze profile spatiation of total and DTPA-extractable zinc forms in alluvial arable soils. Six soil profiles located in the Unisław Basin were analyzed. The soils were classified as alluvial black earths. The alluvial material of the examined soils was overlying calcareous sinter situated 100 cm deep into the ground. Soil samples were analyzed for the grain size composition, reaction, Corg and the $CaCO_3$ content. The total zinc concentration was assessed after mineralization in HF+ $HClO_4$ mixture according to Crock and Severson (1980), while zinc forms extractable with DTPA were assayed with ASA as described by Lindsay and Norvell (1978). The soils did not show symptoms of zinc pollution. Its total, Zn concentrations ranged between 6.25 and 18.78 mg kg^{-1}, while an average content was 11.16 mg kg^{-1}. The analyzed soil samples contained zinc forms extractable with DTPA in amounts fluctuating between 0.32 and 2.6 mg kg^{-1}. The highest concentrations of total and available zinc were noted in the surface horizons of the soils and in the horizons enriched with organic carbon.

Keywords: zinc in soil, alluvial soils, total and DTPA-extractable forms.

PROFILOWE ROZMIESZCZENIE CYNKU W ALUWIALNYCH GLEBACH UPRAWNYCH O NATURALNIE PODWYŻSZONEJ ZAWARTOŚCI WĘGLANU WAPNIA

Abstrakt

Celem pracy była analiza profilowego rozmieszczenia cynku w formie całkowitej i ekstrahowanej DTPA w glebach aluwialnych użytkowanych rolniczo.

dr inż. Agata Bartkowiak, Chair of Soil Science and Soil Protection, University of Technology and Life Sciences, Bernardyńska 6, 85-029 Bydgoszcz, Poland, e-mail: bartkowiak@utp.edu.pl

Przedmiotem badań było 6 profili glebowych zlokalizowanych na terenie Basenu Unisławskiego. Gleby te sklasyfikowano jako mady czarnoziemne. Materiał aluwialny badanych gleb zalegał na martwicy wapiennej, która występowała na głębokości ok. 100 cm. Z podstawowych właściwości w analizowanych próbkach glebowych oznaczono: uziarnienie, odczyn, zawartość C- org. oraz $CaCO_3$. Całkowitą zawartość Zn oznaczono po mineralizacji w mieszaninie kwasów HF+ $HClO_4$ metodą Crocka i Seversona (1980), natomiast formę ekstrahowaną DTPA metodą LINDSAYA i NORVELLA (1978), z zastosowaniem metody ASA. Badane gleby nie wykazywały zanieczyszczenia cynkiem, którego całkowita zawartość wynosiła 6.25–18.78 mg kg^{-1}. Zawartość cynku ekstrahowanego DTPA wahała się od 0.32 do 2.6 mg kg^{-1}. Największe ilości cynku całkowitego i przyswajalnego odnotowano w poziomach powierzchniowych analizowanych gleb oraz w poziomach wzbogaconych w węgiel organiczny.

Słowa kluczowe: cynk w glebie, gleby aluwialne, formy całkowite i ekstrahowane DTPA .

INTRODUCTION

Zinc is a widespread element in nature. It is found in compounds incidentally released to the environment, but it is also an ingredient of mineral fertilizers, pesticides and waste substances applied in agricultural practice. Because of the physiological functions it plays in live organisms, zinc is considered an essential element in nutrition of plants and animals (ALLOWEY 2004). However, any concentration higher than allowable can impair the biological activity of soil. Zinc can be toxic to plants due to zinc compounds accumulating in their vegetative and generative parts, causing adverse effects on the yield volume and quality of crops (ROSZYK et al. 1988). Secondary to this, a threat to higher organisms appears. Similarly to other trace elements, the mobility of zinc in soil and its ability to form bonds depends on the soil sorption capacity, i.e. soil physical and chemical properties (DUBE et al. 2001). High zinc mobility in soil creates a risk of its excessive uptake by plants (KABATA-PENDIAS, PENDIAS 2001, TERELAK , TUJAKA 2003). The degree of tolerance of plants towards zinc depends mainly on soil factors, such as reaction, fractional composition and organic matter content, as well as other conditions, e.g. zinc form and plant species (BARAN 2009, 2011, SPIAK et al. 2000).

The objective of the study was to investigate the profile spatiation of total zinc and its forms extractable with DTPA in profiles of alluvial arable soils with a naturally elevated content of calcium carbonate.

MATERIAL AND METHODS

The subject of this research consisted of six soil profiles located in the Unislaw Basin, and sampled in 2009. Those soils are classified as Mollic Limnic Fluvisol (Calcaric) – profiles 1 and 2, Limnic Epigleyic Phaeozem

– profile 4 and Epigleyic Limnic Fluvisol (Calcaric) – profile 6 (IUSS WRB 2006). The surface (Ap) and subsurface soil horizons (Aa) were composed of mineral alluvial depoists, in which various mineral and organic limnic materials (Lc) were embedded. Soil samples were taken from morphologically distinct layers. They were air-dried and passed through a 2 mm mesh. The fractions with grains finer than 2 mm were separated for the fractional composition according to Jackson (Gonet and Cieśla 1988). The objective was to remove humus, carbonates and free iron oxides. Afterwards, the samples were analyzed for the content of specific fractions from 2 mm to 0.05 mm, using the sieving method, while the share of particles less than 0.05 mm large was determined with the pipette method (Soil Survey Investigations 1996).

Beside the above analysis of soil fractions, the samples were checked for active acidity in H_2O and exchangeable acidity in 1M KCl. Potentiometric assays were performed with a CPC-551 pHmeter (Lityński et al. 1976), concentrations of organic carbon were assessed with the use of a Dutch SKALAR TOC, and the $CaCO_3$ content was determined with the volumetric method according to Schleiber (Lityński et al. 1976). The total zinc concentrations were assayed after mineralization of samples in a mixture of HF and $HClO_4$, as described by Crock and Severson (1980), while the Zn forms easily available and extractable with DTPA were determined according to Lindsay and Norvell (1978). The zinc total content and mobile forms were assayed with atom absorption spectroscopy on a Philips PU 9100X spectrometer. The reliability of the results was attested against SV-M certified material. Additionally, control samples were run, which were analyzed in the same way as the investigated samples. All the determinations were made in triplicates. The results are presented as arithmetic means. Possible correlations between the results were checked with the aid of Statistica software. A correlation matrix of the analyzed factors was based on the Pearson's correlation coefficients using $p< 0.05$ to indicate the 95% probability levels.

RESULTS AND DISCUSSION

Basic physicochemical properties of the soil samples are presented in Table 1. As evidenced by the data, the soils had neutral or alkaline reaction. Thus, pH values expressed in pH/H_2O ranged between 7.30 and 7.87, while those determined in 1M KCl varied from 6.88 to 7.48. The measured values were influenced by high amounts of $CaCO_3$, which made up as much as 76.1% of the material in the limnic horizons. High concentrations of calcium carbonate were shown in the ploughable humus horizons, which contained on average 22.0% of this compound. The above accumulation of carbonates could have been caused by the capillary rise of groundwater saturated with calcium ions to the topsoil. Another possible reason was frequent application

Table 1

Some physicochemical properties of the soils

Profile no	Horizon	pH		Corg	$CaCO_3$	Fraction < 0.002 mm
		H_2O	1M KCl	(g kg^{-1})	(%)	
I	Ap	7.67	7.03	55.8	16.2	48.3
	Ld	7.76	7.12	77.3	29.8	70.6
	Lc	7.51	6.88	195.2	36.7	71.4
	Lm1	7.86	7.24	30.6	59.5	70.6
	Lm2	7.86	7.39	9.5	9.8	61.2
II	Ap	7.59	7.13	63.9	21.8	63.9
	Ah	7.68	7.15	65.9	27.2	60.2
	Ld	7.64	7.17	63.9	40.2	81.5
	Lm1	7.59	7.2	24.4	68.4	47.6
	Lm2	7.63	7.14	59.8	46.0	78.3
	Lc	7.64	7.16	112.9	56.5	44.1
	Lm3	7.65	7.2	14.7	51.6	35.5
III	Ap	7.84	7.41	60.9	24.4	40.5
	Ah1	7.57	7.27	65.7	25.6	38.7
	Ah2	7.26	6.96	63.1	5.3	11.4
	Cr	7.61	7.09	65.8	2.4	6.8
	Ld1	7.68	7.14	7.9	8.5	35.0
	Ld2	7.75	7.30	9.7	39.8	29.9
IV	Ap	7.60	7.30	59.4	26.5	51.0
	Ah	7.68	7.27	19.7	6.7	18.3
	Cr	7.87	7.26	4.9	4.5	32.9
	Cr	7.79	7.16	5.3	0.6	31.9
	Ld	7.86	7.41	1.4	12.1	42.7
V	Ap	7.60	7.33	80.3	23.6	60.0
	Ah	7.53	7.26	78.0	24.9	64.5
	Ld	7.53	7.21	65.0	39.1	57.2
	Lc	7.67	7.4	46.5	48.7	66.0
	Lm	7.57	7.48	14.4	76.1	61.9
VI	Ap	7.38	7.20	50.2	15.9	66.5
	Ah	7.37	7.30	5.1	69.3	29.3
	Ld1	7.37	7.3	29.0	35.2	651
	Lm	7.42	7.25	2.3	70.1	58.1
	Ld2	7.44	7.30	4.1	20.5	23.0
	Ld3	7.46	7.31	2.8	40.6	19.4
	Ld4	7.46	7.35	2.2	37.5	16.2

of agronomic measures, especially ploughing. The amount of organic carbon ranged from 1.4 g kg^{-1} to 195.2 g kg^{-1}. Different concentrations of organic carbon were probably caused by the location of the sampling site in the profile, which can be considered typical for multilayer systems of alluvial soils. Accumulation of organic matter is most strongly determined by the type and kind of soils, although the differentiation of this parameter is also attributable to different land use (PRANAGAL 2004, SKŁODOWSKI 1994).

Our analyses of the fractional composition of the samples revealed that the content of clay particles (∅ < 0,002 mm) ranged from 6.8 to 81.5%. According to the WRB (2006), the analyzed samples were rich in clay (c) and silty clay (ipł). High concentrations of clay, such as found in the examined soils, confirm that stagnant waters create conditions suitable for sedimentation (MYŚLIŃSKA 2001). In turn, a high share of sands could indicate an intensive activity of running water and/or streams from melting continental glaciers. Such runoff could wash off finer fractions from surface clay horizons.

The soils analyzed herein did not manifest symptoms of zinc pollution, with the Zn total concentration between 6.25 and 18.78 mg kg^{-1}, and the average content 11.16 mg kg^{-1} (Table 2). Similar values were determined by JAWORSKA and DĄBKOWSKA-NASKRĘT (2012) in agricultural luvisols. According to TERELAK et al. (2000), an average zinc concentration in soils is 23.3 mg kg^{-1} in the Province of Kujawy and Pomorze, and 32.4 mg kg^{-1} in whole Poland. The highest concentrations of zinc were found in the humus horizons enriched with organic matter. KABATA-PENDIAS and PENDIAS (2001) confirmed that organic matter has a distinct ability to bind zinc. Our statistical analysis of the results revealed a relationship between the content of Zn ions and organic matter (r = 0.408 p < 0.05) – Figure 1. The presence of zinc in soils is mainly connected with its concentration in the parent rock and their abundance in iron and clay minerals (CZARNOWSKA 1984, 1996). Alluvial soils are those of the highest changeability of zinc concentrations, both spatial and the profile one. As for alluvial soils in the Lower Vistula Valley, their content of zinc is mostly dependent on the site (distance from the main stream) and fractional composition. KOBIERSKI and PIOTROWSKA (2010) reported that alluvial soils of the Unisław Basin located 50, 200, 600 and 900 m away from the Vistula riverbed and containing from 7 to 31% of clay fraction had between 30.1 and 228.5 mg kg^{-1} of total zinc. Flood sedimentation of fine material brought by the river caused a significant reduction of impurities transported to the estuary. This is why periodically flooded lowlands are reservoirs of collected suspensions and their heavy metals (TAYLOR 1996). Moreover, specific genesis of soils developed from alluvial sediments (sedimentation processes) affects the profile differentiation of those metals (DĄBKOWSKA-NASKRĘT 1994, DĄBKOWSKA-NASKRĘT, KĘDZIA 1996, ORZECHOWSKI, SMÓLCZYŃSKI 2010).

The region of the Unisław Basin has long-lasting agricultural tradition. The soils in this area present high production potential and are intensively cultivated, which changes their properties considerably. Fertilizers and plant protection preparations can raise the levels of heavy metals in such soils.

Table 2

Total content and DTPA-extractable forms of zinc in the soil samples

Profile no	Horizon	Total content	Extractable (DTPA)	DTPA / Total content
		(mg kg^{-1})		(%)
I	Ap	14.48	2.3	15.88
	Ld	9.76	0.66	6.72
	Lc	12.25	0.98	8.00
	Lm1	11.23	0.68	6.06
	Lm2	8.68	0.58	6.68
II	Ap	15.13	2.29	15.14
	Ah	15.83	1.68	10.61
	Ld	9.68	0.85	8.78
	Lm1	10.13	0.72	7.10
	Lm2	10.30	0.67	6.50
	Lc	11.38	1.03	9.06
	Lm3	12.00	0.64	5.33
III	Ap	18.58	1.92	10.33
	Ah1	18.78	2.40	12.78
	Ah2	11.78	1.41	11.97
	Cr	6.25	0.70	11.20
	Ld1	9.75	0.51	5.23
	Ld2	7.98	0.48	6.02
IV	Ap	12.63	1.88	14.89
	Ah	7.33	0.58	7.91
	Cr	9.15	0.50	5.46
	Cr	7.43	0.61	8.21
	Ld	7.85	0.45	5.73
V	Ap	14.23	2.60	18.27
	Ah	11.75	2.36	20.09
	Ld	11.03	1.52	13.78
	Lc	11.88	0.96	8.08
	Lm	12.05	0.32	2.56
VI	Ap	16.68	1.80	10.79
	Ah	9.90	0.54	5.45
	Ld1	9.95	0.52	5.23
	Lm	6.65	0.52	7.82
	Ld2	9.93	0.56	5.64
	Ld3	12.98	0.36	2.77
	Ld4	6.53	0.44	6.73

The determined profile spatiation of zinc in the examined soils showed some accumulation of Zn ions in the surface horizons, which probably reflects the anthropogenic changes in that region. The surface horizons contained the highest amounts of total zinc, which were decreasing down the profile.

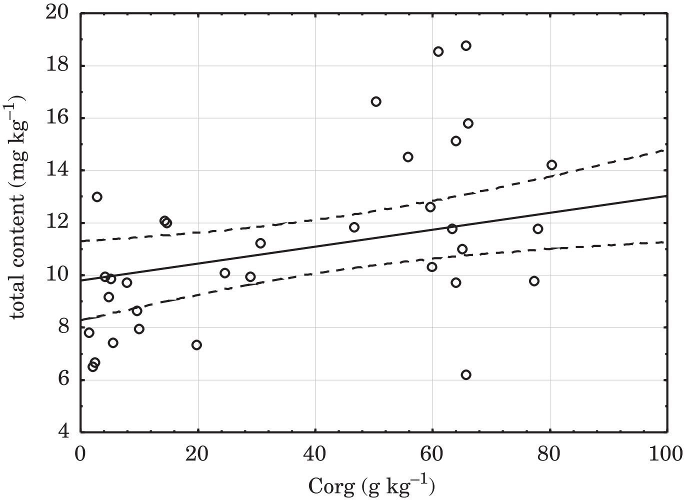

Fig.1 Correlation between the content of total zinc and organic carbon

A similar observation was made by DĄBKOWSKA-NASKRĘT (1994) in her study on arable alluvial soils.

Extraction with diethynene triaminopentaacetic acid (DTPA) was used in order to evaluate the mobility of zinc forms available for plants. Those compounds first accumulate in the humus horizons of many types of soils (NIEMYSKA-ŁUKASZUK, CIARKOWSKA 1999). Zinc is perceived as a mobile element, whose availability and mobility are influenced by a number of factors, such as the content of organic matter, concentration of iron compounds, pH and fractional composition of the soil (ROGÓŻ, GRUDNIK 2004). The soil reaction is seen as one of the most important factors affecting zinc availability (KWIATKOWSKA-MALINA, MACIEJEWSKA 2011). The analyzed soils samples contained from 0.32 to 2.6 mg kg^{-1} of zinc extractable with DTPA, while the corresponding average for all the samples was 1.05 mg kg^{-1}. The share of available forms in the total content of zinc was 2.56%–20.09% (Table 2). The highest amounts of available zinc were found in the surface horizons of the soils and in the horizons rich in organic carbon. A positive and significant correlation was noted between the zinc forms extractable with DTPA and concentrations of organic carbon in the analyzed soil samples (r = 0.505, p<0.05) – Figure 2. A change in soil reaction considerably influenced the concentration and mobility of Zn ions. Higher soil reaction was accompanied by a decrease in the zinc content because of its more intensive binding by iron and aluminum oxides and/or precipitation to less soluble forms. Alkaline reaction of the samples could have decreased concentrations of available zinc, down to the lower threshold of its content in soils with the particle-size distribution typical for clays (KABATA-PENDIAS, PENDIAS 2001).

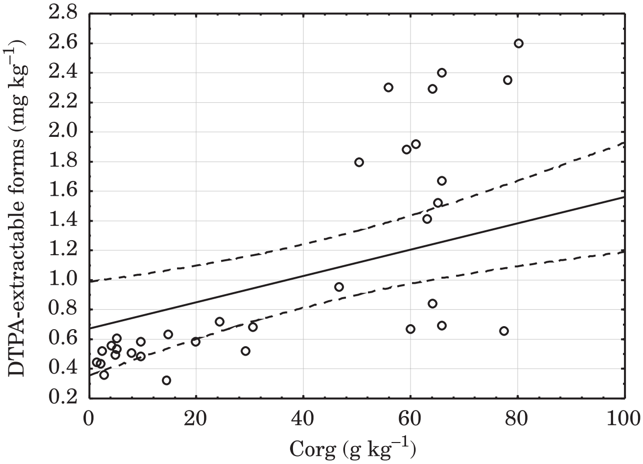

Fig. 2 Correlation between DTPA-extractable forms of zinc and organic carbon

CONCLUSIONS

1. The analyzed soils did not show symptoms of zinc pollution. Its total concentration ranged from 6.25 to 18.78 mg kg^{-1}.

2. The highest concentrations of total and available zinc were noted in the surface horizons of the soils and in the horizons enriched with organic carbon.

3. The profile distribution of zinc in the soils reflected the accumulation of this ion in the surface horizons, which can be a result of anthropogenic changes in that region.

REFERENCES

ALLOWEY B.J. 2004. *Zinc in soils and crop nutrition*. Int. Zinc Assoc., IZA Publications, Brussels

BARAN A., JASIEWICZ CZ. 2009. *The toxic content of zinc and cadmium in soil to different plant species*. Ochr. Środ. Zas. Nat., 40: 157-164. (in Polish)

BARAN A. 2011. *Maize response to toxic zinc content in soil*. Proc. of ECOpole., 5(1): 155-160. (in Polish)

CROCK J.G., SEVERSON R. 1980. *Four reference soil and rock samples for measuring element availability in the Western Energy Regions*. Geochem. Survey Circ., 841:1-16.

CZARNOWSKA K. 1984. *Parent rock effect on the content of heavy metals in soil.* Probl. Post. Nauk Rol., 242: 21-30. (in Polish)

CZARNOWSKA K. 1996. *Total content of heavy metals in parent rock as a geochemical background of soils*. Rocz. Glebozn., supl., 47: 43-50. (in Polish)

DĄBKOWSKA-NASKRĘT H. 1994. *The content of total and DTPA-extractable microelements in selected alluvial soils of the Fordon Wisła Valley and Unislaw Basin*. Zesz. Probl. Post. Nauk Rol., 414: 99-104. (in Polish)

DĄBKOWSKA-NASKRĘT H., KĘDZIA W. 1996. *Content of copper, zinc and nickel in alluvial soils* *from the Lower Vistula River Valley*. Zesz. Nauk. Kom. „Człowiek i Środowisko" PAN, 14: 33-38. (in Polish)

Dube A., Zbytniewski R., Kowalkowski T., Cukrowska E., Buszewski B. 2001. *Adsorption and migration of heavy metals in soil.* Pol. J. Environ. Stud., 10(1): 1-10.

Gonet S., Cieśla w. 1988. *Soil sample dispersion methods for analysis of the silty fraction*. Pr. Kom. Nauk. Pol. Tow. Glebozn., 103, Warszawa, 33 pp. (in Polish)

IUSS Working Group WRB, 2006. *World Reference Base for Soil Resources 2nd ed*. World Reso. Reports, 103, FAO, Rome, pp. 132.

Jaworska H., Dąbkowska-Naskręt H. 2012. *Influence of the Głogów copper works on the content of mobile forms of copper and zinc in arable soils.* J. Elem., 17(1): 57-66. DOI: 10.5601/jelem.2012.17.1.05

Kabata-Pendias A., Pendias P. 2001. *Trace elements in soils and plants*. 3rd. ed., CRC Press.

Kobierski M., Piotrowska A. 2010. *Profile distribution of heavy metals and enzymatic activity in fluvisols of the Vistula River valley, Poland.* Fres. Environ. Bull., 19(2a): 303-311.

Kwiatkowska-Malina J., Maciejewsja A. 2011. *The uptake of heavy metals by plants at differentiated soil reaction and content of organic matter* . Ochr. Środ. Zas. Nat., 49: 43-51. (in Polish)

Lindsay W.L., Norvell W.A. 1978. *Development of a DTPA soil test for zinc, iron, manganese, copper*. Soil Sci. Soc. Am. J., 43: 421-428.

Lityński T., Jurkowska H., Gorlach E**.** 1976. *Agricultural chemical analysis.* PWN, Warszawa, 149 pp. (in Polish)

Myślińska E. 2001. *Organic lands and laboratory methods of organic soil analysis*. Wyd. Nauk. PWN, Warszawa, 208 pp. (in Polish)

Niemyska-Łukaszuk J., Ciarkowska K. 1999. *Zinc, lead and cadmium contents in the profiles of different subtypes of gypsic rendzinas.* Zesz. Probl. Post. Nauk Rol., 467(2): 439-447. (in Polish)

Orzechowski m., Smólczyński S. 2010. *Content of Ca, Mg, Na, K, P, Fe, Mn, Zn, Cu,in soils developed from the Holocene deposits in North-Eastern Poland.* J. Elem., 15(1): 149-159.

Pranagal J. 2004. *The effect of tillage system on organic carbon content in the soil*. Ann. UMCS , Sect. E, 59(1): 1-10. (in Polish)

Rogóż A., Grudnik J. 2004. *Assessment of trace element pollution of soil and root crops*. Ecol. Chem. Engin., 11(8): 775-785.

Roszyk E., Roszyk S., Spiak Z. 1988. *The zinc amount toxic for plants contained in soils*. Rocz. Glebozn., 39: 57-69. (in Polish)

Skłodowski P. 1994. *Influence of soil use on transformation of organic matter*. Rocz. Glebozn., 45(3/4): 77–84. (in Polish)

Soil Survey Investigations, 1996. *Soil survey laboratory methods manual*. Raport No 42, v.3.0.

Spiak Z., Romanowska M., Radoła J. 2000. *The content in soils toxic to different species of cultivated plants.* Zesz. Probl. Post. Nauk Rol., 471: 1125-1134. (in Polish)

Taylor M. 1996. *The variability of heavy metals in floodplain sediments: a case study from mid-Wales*. Catena, 28: 71-87.

Terelak H., Motowicka-Terelak T., Stuczyński T., Pietruch c. 2000. *Trace elements (Cd, Cu, Ni, Pb, Zn) in agricultural soils of Poland.* IUNG, Warszawa, 69 pp. (in Polish)

Terelak H, Tujaka A. 2003. *The content of trace elements in agricultural soils of Podkarpacki Region.* Zesz. Probl. Post. Nauk Rol., 493: 245-252. (in Polish)