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VARIABILITY OF ZINC CONTENT IN SOILS IN A POSTGLACIAL RIVER VALLEY – A GEOCHEMICAL LANDSCAPE APPROACH*

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Abstract

The paper presents the research results on the relation between the contents of total zinc and its bioavailable form (Zn_a) and physicochemical properties of soil carried out along three catenas in the postglacial valley of the middle Łyna River, in NE Poland. We focused on topographical factors to determine the amount of Zn in the soil in relation to specific geochemical landscape types. The analyzed soil showed a relatively low level of soil pollution with Zn and did not exceed the threshold values for soil contamination with Zn. The average Zn content amounted to 45.75 mg kg^{-1} d.m. and ranged from 8.80 to 176.26 mg kg^{-1} d.m. The heavy metal content in the soil was related to organic matter and clay fraction, while it was inversely proportional to the share of sandy fraction. Distribution of zinc showed variability due to factors derived from topography, soil heterogeneity in the river valley as well as fluvial processes taking place within the floodplain. Different geochemical landscapes showed depressive trends in both Zn and Zn_a contents along the catenas. It diminished from eluvial to transeluvial landscapes and increased again to superaqual landscape. Depressions after former river channel were favorable for the Zn_a accumulation. The most abundant in Zn_a were upper horizons of Fluvisols in superaqual landscape (45.12 mg kg^{-1}) filling overgrown and terrestialized floodplain lakes. The share of Zn_a was the highest in organic horizons of Fluvisols and achieved 51.4% of total Zn**.** The nature and power of functional links between the heavy metal mobility and the soil properties were determined with multivariate statistics and GAM models. Applied ordination statistics confirmed its usefulness in soil factor analyses.

Keywords: zinc, geochemical background, soil, river valley, geochemical landscape.

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ZMIENNOŚĆ ZAWARTOŚCI CYNKU W GLEBACH MŁODOGLACJALNEJ DOLINY RZECZNEJ W ASPEKCIE KRAJOBRAZÓW GEOCHEMICZNYCH

Abstrakt

W pracy przedstawiono wyniki badań dotyczących związku między całkowitą zawartością cynku i jego formą biodostępną (Zn_a) a fizykochemicznymi właściwościami gleb. Badania prowadzono w trzech katenach glebowych w środkowym odcinku młodoglacjalnej doliny Łyny w NE Polsce. Skupiono się na czynnikach topograficznych determinujących ilość cynku w glebach w odniesieniu do typologii krajobrazów geochemicznych. Stwierdzono stosunkowo niski poziom zanieczyszczenia badanych gleb cynkiem, którego zawartość nie przekraczała wartości progowych. Zawartość cynku wahała się od 8,80 do 176,26 mg kg^{-1} s.m. (średnio 45,75 mg kg^{-1} s.m.). Zawartość tego mikroelementu była wprost proporcjonalna do zawartości materii organicznej i frakcji ilastej, natomiast odwrotnie proporcjonalna do frakcji piaszczystej. Rozmieszczenie cynku wykazywało zmienność ze względu na czynniki topograficzne, sekwencję gleb w dolinie rzecznej, a także procesy fluwialne w obrębie terenów zalewowych. W sekwencji krajobrazów geochemicznych, tj. wzdłuż katen, obydwie formy cynku wykazywały trend depresyjny: ich zawartość zmniejszała się od krajobrazu eluwialnego do transeluwialnego i ponownie wzrastała w krajobrazie superakwalnym. Akumulacji Zn_a sprzyjały obniżenia po byłym korycie rzeki. Najbardziej zasobne w Zn_a były powierzchniowe poziomy mad rzecznych w krajobrazie superakwalnym (42,12 mg kg^{-1}). Udział Zn_a w stosunku do całkowitej formy tego mikropierwiastka był najwyższy w powierzchniwych poziomach gleb limnowo-saprowych (51,4%). Charakter i siłę powiązań między mobilnością cynku i właściwościami gleb ustalono na podstawie statystyki wielowariantowej wymiarowej PCA i modelu GAM. Zastosowane techniki ordynacyjne potwierdziły ich przydatność w analizach czynników glebowych.

Słowa kluczowe: cynk, tło geochemiczne, gleba, dolina rzeczna, krajobraz geochemiczny.

INTRODUCTION

Zinc belongs to the natural components of soil, and its content depends primarily on a type of parent material and soil-forming processes. Zinc, like other heavy metals in soil, can occur in the form of free metal ions, metal adsorbed onto organic and inorganic complexes, and metal bound to organic and inorganic particulate matter (ALLOWAY 2005). The mean total Zn content in the lithosphere is estimated to be 80 mg kg^{-1} d.m. and most of its surface soil is characterized by Zn levels within the range 17-125 mg kg^{-1} d.m., mean 64 mg kg^{-1} d.m. (ALLOWAY 2005). According to IUNG (KABATA-PENDIAS et al. 1993) the natural content of Zn in Polish soils, amounts to *ca.* 32.7 mg kg^{-1} d.m. and shows a very high degree of purity (98.5%). In north-eastern Poland, an average Zn content in soils has been reported from 29.4 (TERELAK 2001) to 48.8 mg kg^{-1} d.m. (NIESIOBĘDZKA 2001). Soil derived from sands do not usually contain more than 30 mg of Zn kg^{-1} of d.m., from sandy loams about 60 mg of Zn kg^{-1}, and from clay loams or clay more than 80 mg of Zn kg^{-1}.

As it is widely reported (FOSTER, CHARLESWORTH 1996, DOMAŃSKA 2009, DU LAING et al. 2009, DIATTA 2013), heavy metals, including Zn, show decreased or increased mobility in soil in relation to the geological background of a given area. The geochemical variability of soil within river valleys results from topographical and hydrological factors. The lateral migration pattern of elements in soil led to the geochemical landscape classifications developed in the mid sixties of XX century by Russian pedologists such as Glazovskaya and Perel'man (FOSTERSQUE 1980, WICIK OSTASZEWSKA 2012). Thus, considerable differences in the share of Zn and soil parameters, e.g. particle size in particular soil genetic levels are anticipated between eluvial and/or transeluvial landscapes representing upper parts of valley slopes with a deep groundwater table and superaqual and/or subaqual landscapes associated with alluvial floodplains (NIESIOBĘDZKA 2001, DIATTA 2013). Factors controlling the potential availability of zinc are also complex. The biologically available form of Zn (HCl-extracted) can be site-specific, related to particular physicochemical characteristics of the soil or specific mixed contaminants (FOSTER, CHARLESWORTH 1996, BIRCH et al.1999).

The nature of the spatial variability of heavy metal accumulation in alluvial soil is under a direct influence of river activity and diversified by conditions of sedimentation (CZARNOWSKA et al. 1995, MIDDELKOOP 2000, WALLING et al. 2003, CISZEWSKI et al. 2004, OBOLEWSKI, GLIŃSKA-LEWCZUK 2013), particularly during flooding periods (ZHAO et al. 1999). Results from the research on the distribution of heavy metals across floodplains indicates a decrease in Zn concentrations in soils with an increasing distance from the active river channel (MIDDELKOOP 2000, WALLING et al. 2003, CISZEWSKI et al. 2004). In lowland meandering river valleys that distribution may be distorted due to other various water bodies (old -river channels, floodplain lakes) playing the role of sinks in the river landscape (GLIŃSKA-LEWCZUK et al. 2009, OBOLEWSKI, GLIŃSKA-LEWCZUK 2013).

The objective of the present study is the identification of spatial differences in zinc content along soil catenas in the postglacial river valley, which would indicate landscapes where the metal levels were naturally higher than in the others. The investigation on the factors limiting total Zn and its available form have been recognized in the valley of the middle Łyna River in north-eastern Poland.

MATERIAL AND METHODS

Study site

The present study was located in the free-flowing section of the Łyna River in north-eastern Poland, 25 km north of Olsztyn - the largest city in the Warmia and Mazury region (Figure 1). It flows northward to the Pregoła River in the Kaliningrad District (Russia).

Contemporary land relief of the Łyna River catchment shows a young-glacial character, formed as a result of melted glacial waters after the Pomeranian stage of Würm glaciation (Pleistocene). Absolute altitudes come to 75-90 m a.s.l. with relative excess about 20-25 m above the river water. The

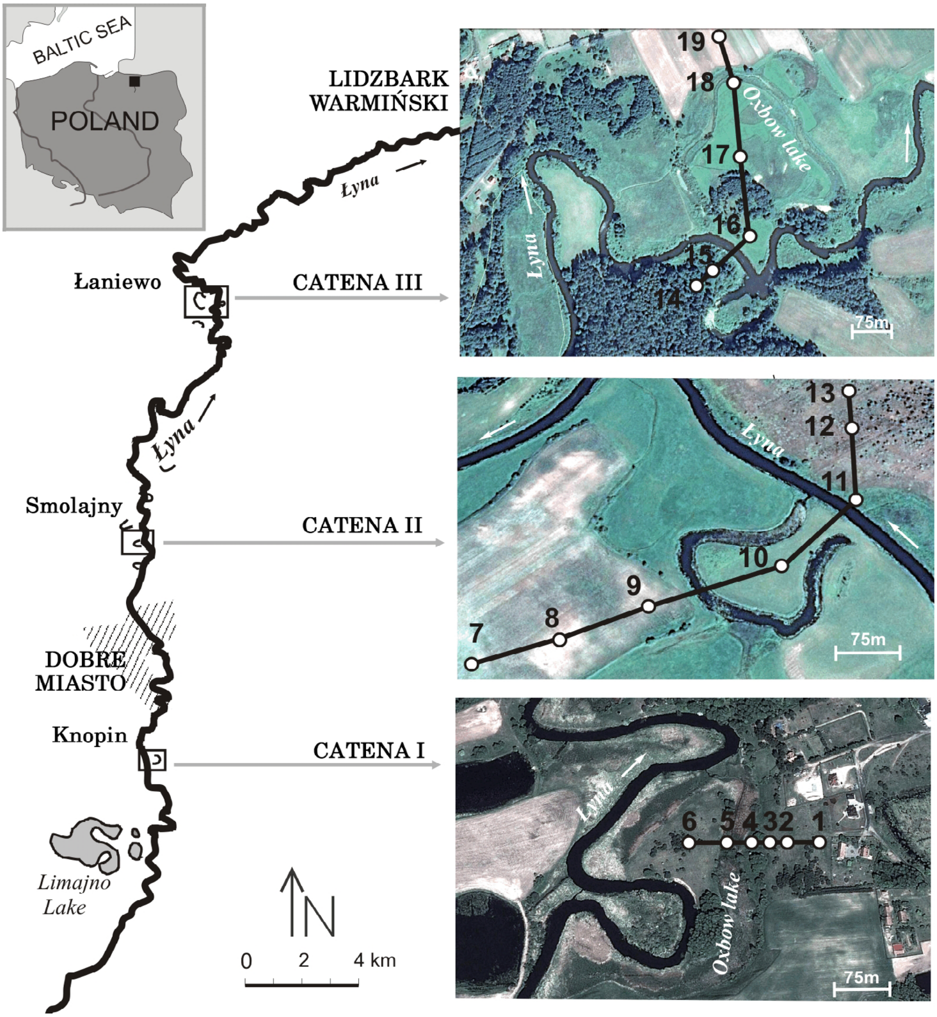

Fig. 1. Location of the study area and catenas with numbers of soil profiles

middle part of its catchment covers a mosaic of soils with features characteristic of morainic hills used by agriculture (53%), forests (29%), lakes (7%) and built-up areas (11%).

At the village of Smolajny, the River Łyna drains a 2290 km^2 area. The average river discharge is 14 m^{3}s^{-1}, ranging from 7 m^3 s^{-1} to 35 m^3 s^{-1} (GLIŃSKA-LEWCZUK 2005). An integral part of the valley is a diverse hydrographic system rich in numerous floodplain lakes, waterlogged depressions, near-shore sandbanks, and flood and over-flood terraces. The common feature of those ecosystems is a strong dependence on the river's activity, which water level fluctuations do not exceed 2 m. Flat floodplain areas are covered by short plants (meadows, pastures) that favor the lateral erosion.

Study sites were located in a distance from possible obvious sources of heavy metals (e.g. major roads, industrial or urban areas). Soil used in this study was taken from three catenas located across the Łyna river valley (Figure 1): at the villages of Knopin (catena I – profiles 1-6), Smolajny (catena II – profiles 7-13) and Łaniewo (catena III – profiles 14-19). The distance between external catenas is *ca.* 20 km. The distance between single soil profiles ranges from 30 m to 70 m, depending on the valley width and its internal structure (floodplain width, levees, oxbow lakes, slopes etc.) and a soil type. The catenas, perpendicular to the valley axis, reflect conditions of potential migration of Zn within the hypergenesis zone. According to the Typology of Geochemical Integration by Glazovskaya (FORTESQUE 1980) four types of geochemical landscapes have been distinguished: (1) eluvial or transeluvial, (2) eluvial accumulative, (3) trans-superaqual and (4) superaqual. Eluvial landcapes have a good natural drainage, e.g. at flat tops of morainic hills where the fluctuations in groundwater level impose no effect on soil parameters. Trans-eluvial forms, represented by steeper slopes, are susceptible to erosion and transport of matter. The eluvial-accumulative landscape is associated to foot-slopes, where a deluvial cover develops. The superaqual landscapes are related to concave forms in the landscape, where capillary rise supplies the root zone in water. In the conditions of active water exchange (hyporheic zone) soil is rich in immobilized forms of chemical elements (heavy metals) what is typical of trans-superaqual landscapes (WICIK, OSTASZEWSKA 2012)

Soil sampling and analytical procedures

In the analyses, 57 soil samples taken from characteristic genetic horizons from 19 soil profiles have been used. The samples were transferred to the laboratory in separate bags and then air-dried for further physical and chemical analyses. Particle size distribution was determined aerometrically following the Casagrande's method modified by Prószyński. Texture classes were determined according to Polish Society of Soil Science using USDA standards (PTG 2009). To obtain the content of organic matter, all samples were combusted at 550°C. Soil pH was measured in KCl with a potentiometer. Calcium carbonate was determined with the gasometrical method using the Scheibler's device.

The content of total Zn in all of the soil samples was determined after digestion of the 3:1 solution of nitric and hydrochloric acids (aqua regia acid) at 150°C (OSTROWSKA et al. 1991). To determine the available form of Zn (Zn_a) soil was extracted in 1M HNO_3 (mineral samples) or 0.5 M HNO_3 (organic samples). In every extract the concentrations of Zn or Zn_a were determined in triplicate using AAS technique in a certified laboratory. The detection limits for Zn were 1 ppm. All the metal contents are given in mg kg^{-1} of dry mass. In order to interpret the results of soil tests in terms of Zn contamination in the middle Łyna River valley, natural metal levels in the soil have been determined. Geochemical background of Zn in soil was calculated based on its average content in parent material from depths > 90 cm and determined according to the Czarnowska method (CZARNOWSKA 1996).

Statistical procedure

To assess the general differences among groups of soils texture classes, pH_{KCL}, organic matter were subjected to non-parametric analysis of variance with the use of Kruskal-Wallis test (K-W; $P \leq 0.05$). The precise statistical significance of differences in analyzed Zn and Zn_a among the studied objects was determined with the Dunn's test ($P < 0.05$). Except of the Dunn's test, statistical analyses were performed using the software package Statistica 10.0 PL for Windows.

In order to identify the primary environmental gradients affecting Zn contents in soil a multivariate statistical analyses involving a linear indirect method of Principal Component Analysis (PCA) was performed. The data was transformed to logarithms log(n+1) to satisfy conditions of normality. For the ordination analysis Canoco 4.5 software was used (TER BRAAK, ŠMILAUER 2002). The generalized additive model (GAM, $P \leq 0.001$) has been provided towards correct interpretation of ordination diagram computed for the Zn contents in relation to physical properties of soil. Variables that were not significant ($P \leq 0.05$) were dropped from the model. The Akaike Information Criterion (AIC) was given in the model, as well. The GAM built here was useful to model Zn content in soil and to predict its spatial variations in the river valley.

RESULTS AND DISCUSSION

Soil characteristics

In the middle Łyna river valley, according to the Polish Soil Classification system (*Polish soil ...* 2011), alluvial soil derived from sands and silts as well as peat-mud soils prevails. In the areas adjacent to the bottom of the valley one may found luvisols and deluvial soil derived from loams, silts and clays. The slope of the valley is also covered by rusty soil, arenosols and deluvial soils derived from sands. According to the WRB classification of soils (IUSS Working Group WRB 2006), the Łyna River valley is covered by Mollic Fluvisoils, Haplic Fluvisols and Limnic Sapric Histosols, whereas slopes of the valley by Haplic Luvisols, Gleyic Luvisols, Cumulinovic Arenosols, Mollic Gleysols (Colluvic), Brunic Arenosols (Distric) and Haplic Arenosols (Table 1).

Changes in soil properties along the soil profile in a variety of locations within toposequences and their accumulation series indicate relations involving matter transport and accumulation. In most soil types in the elu-

Table 1

Chosen properties of soil types in relation to the Zn content and its availability on the background of geochemical landscape units

Geochemical landscape unit*	Profile No	Soil type	Hori-zon	Depth (cm)	Texture class	pH_{KCl}	OM	$CaCO_3$	% fraction of diameter (mm)				Zn_t average	Zn_a average	Availability of Zn (%)
							(%)		>2	2-0.05	0.05-0.002	<0.002	(mg kg^{-1})		
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Eluvial/ transeluvial	1	Brunic Arenosol (Distric)	A	0-26	S	4.1	1.24	0.13	0	89	9	2	19.27	5.11	26.5
			Bv	26-120	S	5.4		1.15	0	88	11	1	20.56	2.54	12.4
			C	120-150	S	7.6		0.17	0	96	3	1	21.80	1.32	6.1
	19		Ap	0-26	S	4.4	1.53	0.09	0	84	16	0	37.67	4.90	13.0
			Bv	26-80	S	5.6		0.09	0	95	3	2	12.80	2.72	21.3
			C	80-150	S	7.1		0.0	0	92	8	0	14.52	2.96	20.4
	2	Haplic Arenosol	A	0-28	S	4.3	1.12	0.17	0	89	9	2	117.47	4.79	4.1
			C	28-150	S	8.3		6.13	0	100	0	0	63.20	2.17	3.4
	13		A	0-22	S	4.4	1.03	0.0	5	95	5	0	19.53	3.82	19.6
			C	22-150	S	4.5		0.0	0	99	1	0	19.87	4.06	20.4
	7	Haplic Luvisol	Ap	0-31	L	6.9	4.02	0.0	0	47	42	11	102.33	28.99	28.3
			Et	31-56	SiL	6.2	-	0.0	0	12	62	26	55.67	8.44	15.2
			Bt	56-102	SiC	6.3	-	0.0	0	7	43	50	48.73	18.98	38.9
			C	102-150	SiCL	6.4	-	0.0	0	8	52	40	154.80	16.56	10.7
	8	Gleyic Luvisol	Ap	0-33	SL	4.4	2.23	0.0	0	71	23	6	47.33	17.52	37.0
			Et	33-58	SiL	5.1	-	0.0	0	40	53	7	24.47	4.11	16.8
			Bt	58-90	C	5.1	-	0.0	0	16	29	55	44.47	17.62	39.6
			Cg	90-150	HC	6.1	-	0.0	0	10	24	66	42.20	24.41	57.8
Aluvial accumulative	3	Mollic Gleysol (Colluvic)	A	0-68	LS	5.6	2.74	0.13	0	75	21	4	161.87	5.50	3.4
			C	68-150	SiCL	5.7		1.28	0	14	54	32	53.73	12.25	22.8
	9		Ap	0-30	SL	5.1	2.85	0.0	0	71	23	6	15.67	6.08	38.8
			A2	30-56	SiL	5.1	3.69	0.0	0	31	52	17	29.60	7.15	24.2
			A3	56-107	SiL	5.0	1.61	0.0	0	27	53	20	39.80	10.72	26.9
			G	107-150	S	5.8		0.0	45	87	6	7	20.80	5.72	27.5
	6	Cumulinovic Arenosol	A1	0-30	S	7.0	3.12	0.26	0	88	12	0	22.33	3.85	17.2
			A2	30-110	S	7.1	2.79	0.17	0	92	8	0	65.53	5.26	8.0
			2C	110-150	SiCL	7.3		17.45	0	12	59	29	176.26	8.78	5.0
	12		A1	0-30	S	7.3	2.84	0.10	13	91	9	0	22.07	8.24	37.3
			A2	30-110	S	7.2	1.67	0.19	12	91	8	1	33.93	9.31	27.4
			A3	110-150	S	7.0	1.01	0.0	9	90	9	1	24.47	2.37	9.7

cont. Table 1

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Trans-superaqual	14	Haplic Fluvisol	A	0-32	SL	6.5	2.31	0.17	0	55	26	19	85.47	43.89	51.4
			C1	32-90	SL	7.2		1.36	0	57	33	10	27.73	8.61	37.9
			C2	90-150	SL	7.1		1.88	0	67	32	3	33.87	7.38	21.8
	16	Haplic Fluvisol	A	0-18	SL	6.7	2.77	0.17	0	59	41	0	33.33	16.67	50.9
			C1	18-60	SL	7.6		1.11	0	69	29	2	21.00	4.03	19.2
			C2	60-150	S	8.0		1.45	0	89	9	2	14.73	3.03	20.6
	17		A	0-16	SL	6.7	2.52	0.21	0	57	41	2	33.33	13.15	39.5
			C1	16-50	L	7.0		0.26	0	50	41	9	25.93	5.71	22.0
			C2	50-150	SL	7.7		0.85	0	71	27	2	14.00	6.07	43.4
Super-aqual	10	Mollic Fluvisol	A1	0-23	SL	6.9	9.37	0.0	0	55	37	8	54.13	21.29	39.3
			C1	23-90	SiL	6.9	9.91	0.0	0	27	57	16	65.13	17.29	26.5
			AC	90-150	SL	7.5	2.55	1.30	0	66	26	8	25.67	10.02	39.0
	11		A1	0-26	SiL	5.9	18.71	0.0	0	32	53	15	127.13	35.20	27.7
			A2	26-73	SiL	6.1	12.45	0.0	0	24	56	20	96.47	19.54	20.3
			A3	73-100	L	6.4	4.88	0.0	0	45	40	15	36.27	11.23	31.0
			AC	100-150	LS	6.5	2.74	0.0	0	74	22	4	25.80	9.75	37.8
	15		A	0-32	SL	6.5	3.58	0.54	0	56	35	9	93.67	45.12	48.2
			C1	32-90	SL	7.5		1.96	0	62	35	3	32.27	7.27	22.5
			C2	90-150	LS	7.8		1.45	0	83	15	2	9.27	3.59	38.7
	4	Limnic Sapric Histosol	Lc	0-50	L	7.0	10.57	0.00	0	79	21	0	25.73	9.65	37.5
			Oa	50-120	fen peat	6.5	19.73	0.73	-	-	-	-	7.56	3.87	51.2
			C	120-150	LS	7.1		0.85	0	48	40	12	37.93	9.31	24.5
	5		Lc	0-90	SL	6.8	17.52	0.0	0	55	41	4	49.67	17.01	34.2
			Oa	90-117	fen peat	6.5	53.74	0.68	-	-	-	-	29.67	9.92	33.4
			Lcm	117-150	gyttja	6.6		2.83	-	-	-	-	55.00	15.76	28.7
	18		Lc	0-60	SiL	7.2	16.64	1.05	0	33	52	15	68.53	32.85	47.9
			C	60-150	S	7.7		1.28	0	92	8	0	8.80	4.06	46.1

*According to FORTESQUE (1980) after GLAZOVSKAYA (1963) vial landscape (except for Haplic Luvisols), influences horizon A shows the highest acidity, with significantly lower pH (<4.5) and the lowest organic matter content when compared to other landscape units. Despite differences between individual catenas, changes in Zn and Zn_a concentrations are regular. In general, two change patterns occur. The first characterizes catenas, where Zn concentrations are the lowest in autonomous locations, growing steadily downhill all the way to the floodplain. In the second pattern, the fluctuations of concentrations occur involving a clear decrease in Zn contents from the top to the middle slope zones, with a relatively fast increase in its concentrations at the foot-slope and in the floodplain.

Zinc content and natural background values in soil

The average content of Zn in the investigated soil amounted to 47.04 mg kg^{-1} d.m. The average Zn content in soil types distinguished from 19 soil profiles, ranged from 8.80 to 176.26 mg kg^{-1}d.m. (Table 1). Maximal Zn content was noted for Cumulinovic Arenosol at the horizon 2C in profile 6 at Knopin. According to the regulation of the Ministry of Environment in Poland dated of 4 Oct. 2002 on soil quality standards, the soils do not pose a threat to people's health or the environment in terms of zinc content.

The range of Zn_a content amounted from 1.32 to 45.12 mg kg^{-1} d.m. (Table 1). The highest values of Zn_a characterized upper (A) horizons of Haplic Fluvisols and Mollic Fluvisols, in which their availability achieved *ca.* 50% of total Zn. Although a significant correlation between the two forms of Zn was stated (r = 0.571 at $P \le 0.001$), a significant variability of both forms were found in terms of soil morphological properties (Figure 2).

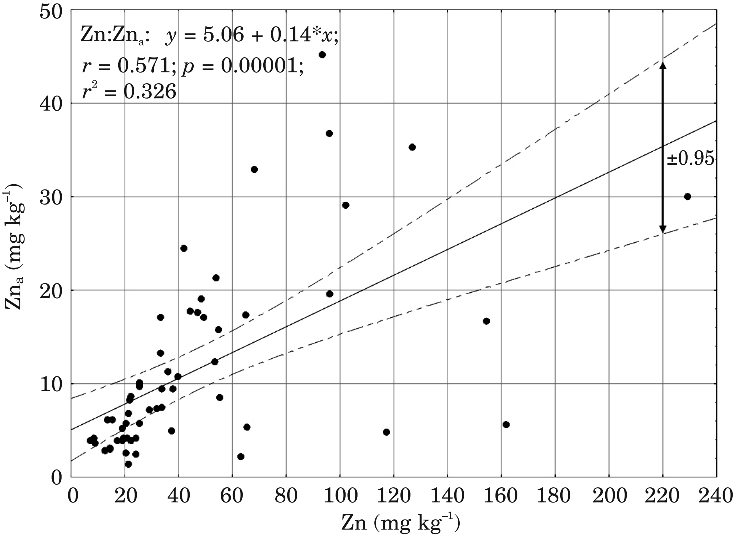

Fig. 2. Relationship between total Zn content and extractable Zn_a in soils of the middle Łyna River valley

Table 2

Zn content in sedimentary rocks at depths >90 cm in the middle Łyna River valley as reference background levels

Parent rock and a textural group	Number of samples	Average background level (mg kg^{-1} d.m.)
Quarternary clays	3	83.6
Fluvioglacial sands	13	22.3
including:		
loamy sands	4	26.8
sands	9	22.1
Average for all studied samples of parent materials	16	33.8

In order to differentiate between natural and anthropogenic origins of Zn in the valley of the Łyna River the geochemical background of parent material was determined. The average background value for Zn amounted to 33.8 mg kg^{-1}, but some distinct differences among the investigated parent material were noticed (Table 2).

The background value presented for sands was similar to those reported by CZARNOWSKA (1996) and amounted to 22.3 mg kg^{-1}. However, our investigation displayed more than 1.5 times higher background level of Zn for clays (83.6 mg kg^{-1}) in comparison to the values obtained by CZARNOWSKA (49.0 mg kg^{-1}). Nevertheless, our results confirm the data of other researchers (KABATA-PENDIAS et al. 1993, TERELAK 2001).

Zn distribution and soil properties

Both total and available forms of Zn showed somehow sensitivity to many physical and chemical properties of the soil in the investigated section of the river valley (Table 3, Figure 3).

Table 3

Correlation coefficients between physical-chemical properties of soil and the contents of Zn and available Zn_a in investigated soils

Property of soil	Zn	Zn_a
Organic matter	0.430*	0.525*
$CaCO_3$	-0.181	-0.230
pH_{KCl}	-0.199	-0.112
Depth of the soil uptake	0.161	-0.291
Fractions ∅ (mm):		
sand 2.0-0.05	-0.449*	-0.512*
silt 0.05-0.002	0.428*	0.464*
clay <0.002	0.341*	0.419*

The investigated soil properties that significantly influence Zn and Zn_a contents may be put in the following decreasing order: Zn or Zn_a**:** organic matter > silt > clay. Soil organic matter is the main component of the soil solid fraction and a key factor in Zn accumulation. In general, the higher the organic matter content the greater the ability to retain the heavy metal.

Organic horizons of Histosols stated in catena I at Knopin contained from 26 to 55 mg of Zn kg^{-1} d.m. and from 10 to 17 mg of Zn_a kg^{-1} d.m. The content of total Zn in the upper soil horizons was by 30% higher in comparison to the Zn content in mineral subsoil. Available form of Zn in organic horizons dominated more than 3 times over mineral substratum.

A distinct tendency to the zinc decrease down the profiles in Mollic Fluvisols derived from silt (catena II) was observed. Surface horizons contained from 54 to 127 mg of Zn kg^{-1} d.m., whereas parent material *ca.* 25 mg Zn kg^{-1} d.m. (profiles 10 and 11; Figure 1 and Table 1). The share of Zn_a amounted to 20-39% of total Zn and was proportionally distributed in relation to Zn.

Widespread Fluvisols (profiles 16, 17), derived from well-sorted sands in the valley of the Łyna River at Łaniewo were found to have relatively low Zn contents. At soil surface, Zn values achieved 33 mg kg^{-1} d.m., whereas subsurface horizons showed Zn content below 14 mg kg^{-1} d.m. Zn_a content displayed similar values in analogous soils in the catena II at Smolajny. The finest fractions in the catenas have also a distinctly pronounced Zn difference between the silt ($r = 0.428$) and sand fractions ($r = -0.449$), what is the evidence of intensive adsorption of metals to fine particles. The clay minerals have a much greater cation exchange capacity, and thus they have a much greater tendency for immobilizing metal ions such as Zn. The available form of Zn was also related to the clay fraction, however to less extent than the total form of the metal. The fraction of clay was also related to the Zn_a content ($r = 0.419$; $P \leq 0.05$).

The soil's ability to immobilize heavy metals increases with rising pH and peaks under mildly alkaline conditions. The relatively high mobility of Zn was observed in the eluvial unit in acid soils (pH 4.2-6.6), while in alkaline soils (pH 6.7-7.8) Zn became moderately mobile or even immobile. Researchers have reported a statistically significant correlation between soil pH and Zn content but our results do not support this and show no statistically significant correlation (KABATA-PENDIAS et al. 1993, TERELAK 2001).

To assess the relation between Zn content, $CaCO_3$, pH, organic matter and the share of soil fractions, a multivatiate method of PCA was applied (Figure 3). The relationship explained 60.9% of total variation. The first axis explained almost 56.1% of the variance of species-environment relationship, this axis is mainly negatively correlated to gravel, and then to $CaCO_3$, while it is positively correlated mainly with organic matter, and subsequently to Zn and Zn_a. This means that sampling sites situated on the right side of the first axis are characterized by low ability to bound or absorb zinc. On the

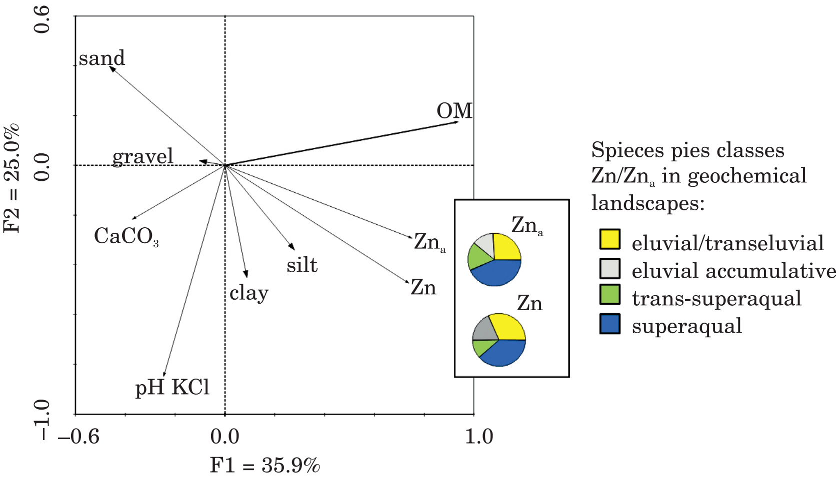

Fig. 3 Biplot of PCA computed for the zinc (Zn and Zn$_a$) and soil properties. Pies classes denote the shares of Zn and Zn$_a$ in the landscape units defined for the Łyna River valley

left side of this axis sampling sites with higher share of OM are shown. This axis could be interpreted as organic matter environmental gradient. The second axis with 16.8% of the variance of species-environment relationship explained is negatively correlated with pH$_{KCl}$, and then fine fractions of silt and clay and positively correlated mainly with sand fraction.

To show the share of Zn and Zn$_a$ in the geochemical landscape units a pies classes graphs have been inserted into Figure 3, where the role of superaqual landscape in Zn immobilization can be seen.

Zn in soils of geochemical landscapes

Figure 4 is shows the distribution of soil samples with sizes proportional to the Zn content based on the PCA standard analysis. Each of them represents one of four geochemical landscape types distinguished for the Łyna River valley. Eluvial and transeluvial (Arenosols, Luvisols) as well as trans-superaqual sites (Haplic Fluvisols) rich in Zn are grouped in the diagram (Figure 4) in the neighborhood of clay and silt, whereas eluvial accumulative and superaqual (Fluvisols) are located near OM. Based on the Zn concentrations and soil properties, a GAM model has been built ($P \leq 0.001$) to present isolines of Zn distribution in relation to soil properties.

Among soils in eluvial and transeluvial landscapes, the metal content was conditioned by physical properties of soil, mainly fine particles. The highest concentrations of Zn were stated in soils derived from clay (profile 7), namely Haplic Luvisol. In the uppermost layer, to a depth of 30 cm, its content amounted to 102 mg kg^{-1} d.m. Beneath the layer, zinc content decreased by 50%. Such a distribution is an effect of a very high content (ca. 50%) of the fraction <0.002 mm. Among soils in the eluvial landscape unit (profiles

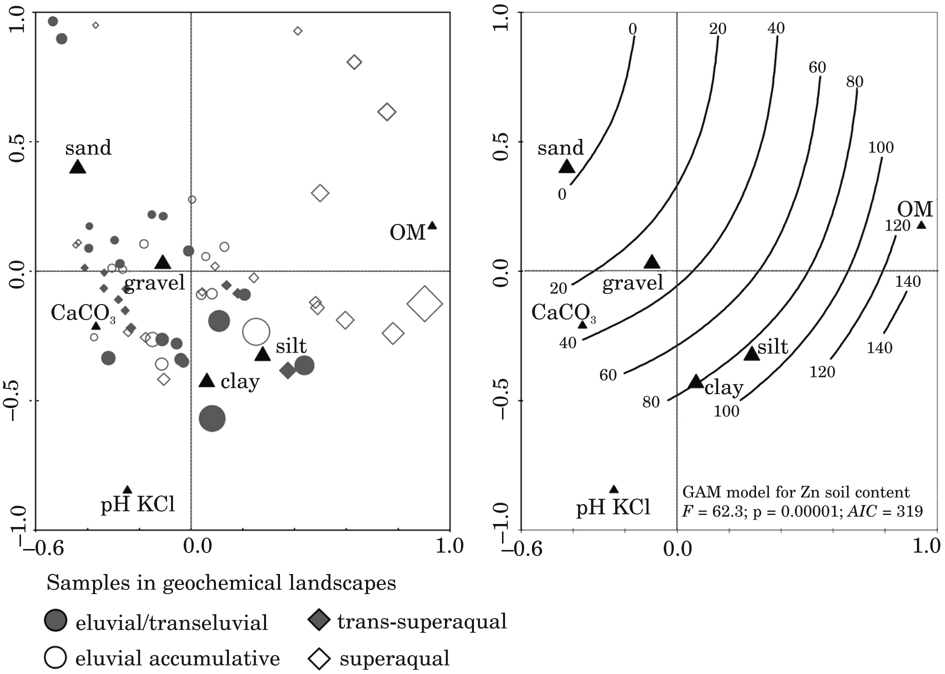

Fig. 4. Variability of Zinc content in soil samples taken from profiles from various geochemical landscape units within the Łyna River valley (left graph). The symbol size is relative to the Zn content in soil. Generalized Additive Model (GAM) computed for the Zn content in relation to physical properties of soil (right graph)

1, 19), rusty soils showed the lowest values of Zn. The fluvioglacial sands are characterized by relatively low contents of Zn (35 mg kg^{-1}) in comparison to the clay of the Quaternary origin (75 mg kg^{-1}). In soils derived from these sedimentary rocks, a correlation between clay fraction and the amount of Zn is positive and statistically significant (r = 0.54). Other researchers have reported the same relationship (Foster, Charlesworth 1996, Dube et al. 2001).

These depressions, in the form of overgrowing floodplain lakes, are common in the study reach (Glińska-Lewczuk 2005). Due to frequent inundations, they receive regular inputs of metals, as well. Existing, filled with alluvium, old-river beds in the catenas I and III accumulated Zn mainly at the upper soil layer (0-30 cm) built of a significant amount of clay (20%) and organic matter (e.g. profile 14, see Figure 1). Within these depressions, Zn showed the highest values (60-80 mg kg^{-1}) among all of the profiles across the floodplain. Available fraction of Zn was also the highest in those depressions and amounted to 35-42 mg kg^{-1}. Accumulation of Zn is indicative then, for any storage properties of e.g. oxbow lakes playing a role as a sink in a river valley. Zn content in their bottom sediments has been reported at a level of 65.7 mg kg^{-1} d.m (Glińska-Lewczuk et al. 2009).

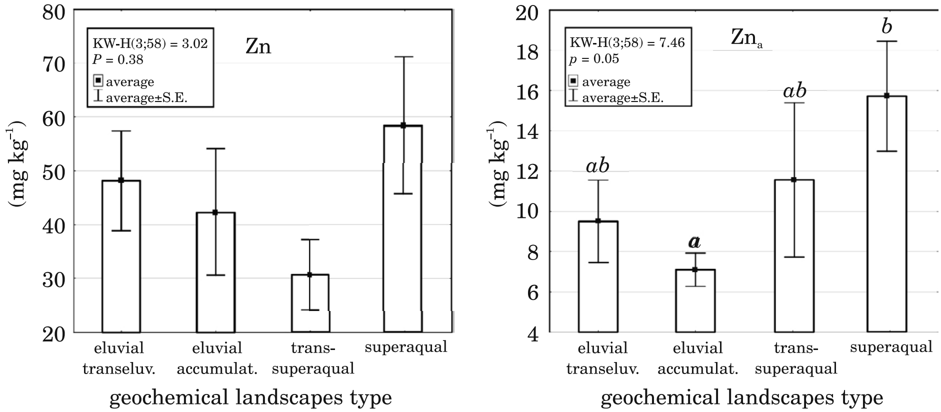

Fig. 5. The distributions of Zn and available Zn form (Zn_a) across the middle Łyna River valley Vertical bars denote standard error of mean (±SE). Statistically different groups of soils classified to a geochemical landscape type in the Dunn's test is denoted with different letters ($P \leq 0.05$)

Different geochemical landscapes showed depressive trends (see Fortescue 1980), for both Zn and Zn_a contents along three studied catenas (Figure 5). Values of Zn diminished from eluvial/transeluvial landscapes (48 mg kg^{-1}) to trans-superaqual (31 mg kg^{-1}) and increased again in superaqual landscapes (58 mg kg^{-1}). The superaqual landscape was favorable for the Zn_a immobilization (15 mg kg^{-1}), while eluvial accumulative landscape was characterized by the higher Zn mobility (7 mg kg^{-1}). Soil profiles (Fluvisols) adjacent to the river channel, and within the reach of the river flooding, showed stabile Zn concentrations (38 mg kg^{-1}). Evenly distributed Zn contents within the floodplain, indicate no significant metal contamination by the river activity in spite of possible influence of the towns located upstream the Łyna river, which are potential sources of soil contamination e.g. with municipal sewage.

CONCLUSIONS

The distribution of Zn in the middle Łyna river valley shows variability due to many factors derived from the topographical location of soil, soil heterogeneity within the river valley as well as fluvial processes taking place within the floodplain. An analysis of the geochemical landscape types applied to the migration of Zn in conditions of postglacial area enabled the recognition of specific variability of landscape structure and functioning eluvial, illuvial and deluvial processes within a single catena. Therefore, upland units are characterized by matter outflow, transitional slopes by matter transportation, with local accumulation or denudation, while spots located at foot-slopes, on the valley bottom and in subordinate depressions, are characterized by accumulation. A geochemical gradient found on the base of Zn in a postglacial river valley appears to have a depressive trend in terms of Zn and Zn_a contents along the catenas. It diminished from eluvial to transeluvial landscapes and increased again in the superaqual landscape. The nature and power of functional links between the metal mobility and the soil properties can be analyzed with multivariate statistics and supported by GAM models.

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