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CONTENT OF SELECTED TRACE ELEMENTS AND EXCHANGEABLE CATIONS IN SOILS OF THE BARYCZ RIVER VALLEY*

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Abstract

In many ways, the Barycz Valley is a unique region. For one thing, it contains the highest number of fish ponds in Poland. Secondly, it is free from heavy industry and large cities. Thus, this region may be considered considerably clean, and the observed concentrations of trace elements are typical for non-degraded environments. There is, however, a threat of excessive accumulation of trace elements such as Zn, Pb and Cu in waters of the rivers in the Barycz drainage basin, received from point sources, and especially supplied with wastewater. These rivers play a very important role; namely, they are the source of water for filling up numerous ponds (Marek 1989). On the other hand, any seepage of river waters into the groundwater may cause excessive concentrations of trace elements in soils near the ponds.

The objective of the study was to analyse and assess sorption properties of sandy soils used as hay meadows. As the study was conducted in a special bird protection area (SBP) included in the European Ecological Network Nature 2000, special attention was paid to the content of selected trace elements. The following analyses were performed on the collected soil samples: particle size distribution, pH in 1 mol KCl dm^{-3}, TOC, N total, content of exchangeable base cations (Ca^{+2}, Mg^{+2}, K^{+}, Na^{+}) and total content of the metals Fe, Mn, Zn, Pb and Cu.

The genesis of the examined soils seems closely linked to the very wet moistened local environment, which significantly influenced the physical and physicochemical soil parameters. These soils were formed in a region crisscrossed by a dense network of watercourses of the Barycz River drainage basin, with strong ominant aquaculture traditions. The sum of base exchange cations (S) and cation exchange capacity (CEC) in the examined soils are strongly affected by the particle size distribution, the fact confirmed by significant positive relationships with the silt fraction and colloidal fraction, and significant negative correlations with the sand fraction. Higher content of Zn, Pb and Cu in surface genetic horizons of the examined soil profiles may point to the anthropogenic origin of the metals. Despite the dominant sandy texture, the soils are characterised by a thick humus horizon, abundant in TOC and TN, which increases their capacity for trace element accumulation. Our assessment of the contamination

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of these soils with Zn, Pb and Cu did not demonstrate any excess in terms of the permissible levels of the trace elements.

Keywords: soil physicochemical properties, soil chemical properties, concentration of trace elements in soils.

ZAWARTOŚĆ WYBRANYCH METALI CIĘŻKICH ORAZ WYMIENNYCH KATIONÓW ZASADOWYCH W GLEBACH POŁOŻONYCH W DOLINIE BARYCZY

Abstrakt

Dolina Baryczy stanowi pod wieloma względami region unikatowy. Występuje tam największe w Polsce skupisko stawów rybnych i brak jest większego przemysłu oraz dużych ośrodków miejskich. Region ten można więc uznać za mało zanieczyszczony, a stwierdzone stężenia pierwiastków śladowych typowe dla środowiska niezdegradowanego. Istnieje jednak niebezpieczeństwo nadmiernego nagromadzenia się pierwiastków śladowych, takich jak Zn, Pb i Cu, w wodach rzek zlewni Baryczy wnoszonych ze źródeł punktowych, szczególnie wraz ze ściekami. Rzeki te pełnią bardzo ważną funkcję, są źródłem wody dla licznych stawów w okresie ich napełniania (Marek 1989), a ich przesiąki dostają się do wód gruntowych i mogą powodować nadmierną koncentrację pierwiastków śladowych również w sąsiadujących ze stawami glebach.

Przedmiotem badań była analiza i ocena właściwości sorpcyjnych piaszczystych gleb czarnoziemnych użytkowanych jako łąki kośne. Ponieważ badania prowadzono na obszarze specjalnej ochrony ptaków (OSO) objętym Europejską Siecią Ekologiczną Natura 2000, zwrócono szczególną uwagę na zawartość wybranych pierwiastków śladowych. Badania wykonano w 6 profilach glebowych usytuowanych na terenie Doliny Baryczy i jednocześnie na obszarze specjalnej ochrony ptaków (OSO). Po opisaniu ich morfologii, z poziomów genetycznych pobrano próbki glebowe, w których wykonano następujące oznaczenia: skład granulometryczny, C-organiczny, pH w H_2O oraz 1mol KCl, zawartość $CaCO_3$, kwasowość wymienną (Hw), zawartość N ogółem, wymienne kationy zasadowe (Ca^{+2}, Mg^{+2}, K^+, Na^+) oraz całkowitą zawartość metali: Fe, Mn, Zn, Pb i Cu.

Genezę powstawania badanych gleb należy wiązać ze środowiskiem silnie uwilgotnionym, które w istotny sposób wpłynęło na ich parametry fizyczne i fizykochemiczne. Gleby te wykształciły się bowiem na obszarach zdominowanych przez hodowlane stawy rybne oraz pokrytych gęstą siecią cieków wodnych zlewni rzeki Baryczy. Zawartość kationów wymiennych zasadowych (S) oraz pojemność kompleksu sorpcyjnego (CEC) w badanych glebach jest ściśle związana z udziałem poszczególnych frakcji granulometrycznych, czego potwierdzeniem są istotne dodatnie zależności z frakcją pyłu i frakcją koloidalną oraz istotne ujemne zależności z frakcją piasku. Większa zawartość Zn, Pb i Cu w wierzchnich poziomach genetycznych analizowanych profilów glebowych może wskazywać na ich antropogeniczne pochodzenie. Badane gleby, mimo dominującego piaszczystego uziarnienia, charakteryzują się dużą miąższością poziomu próchnicznego zasobnego w C-org. i N-og., co zwiększa ich możliwości do akumulowania pierwiastków śladowych. Ocena stopnia zanieczyszczenia analizowanych gleb pod względem zawartości Zn, Pb i Cu nie wskazuje na przekroczenie w nich dopuszczalnych zawartości wymienionych pierwiastków śladowych.

Słowa kluczowe: właściwości fizykochemiczne gleb, właściwości chemiczne gleb, zawartość pierwiastków śladowych w glebach.

INTRODUCTION

Under natural conditions, the amount of trace elements observed in soils is mainly determined by their abundance in the bedrock, intensity of weathering processes and the course of soil formation processes (Kabata-Pendias 1981, Czarnowska, Gworek 1987, Czarnowska 1996, Gworek, Jeske 1996). Analysis of soluble forms of trace elements in soil allows one to foresee threats to the environment due to the incorporation of such elements into biotic elements of the food chain and their migration to groundwater and surface waters (Chojnicki, Kowalska 2009). Abundance of nutrients, in turn, is one of the factors which determine soil fertility. The amount and distribution of nutrients in soil profiles are mostly influenced by the type of bedrock, soil texture and the course of soil formation processes.

A distinguishing feature of the natural environment in the Barycz Valley, resulting from human activity, is the presence of numerous breeding ponds, which were first created in that area in the early 13th century. The development of aquaculture was encouraged by the shallow declines of the River Barycz and its tributaries, the flatness of the area and the presence of numerous earth pits after bog iron exploitation. The early 19^{th} century witnessed expansion of the embankments along the Barycz River, increasing water shortages and a growing demand for arable soils, which all led to a considerable drainage of water from the whole area. Many large fish ponds were liquidated and much of the area was transformed into forests, meadows and arable fields (Ranoszek 1999). Human interference with the natural environment of the Barycz Valley evidently affected the formation of soil types in the region. Next to the sandy sandur hills with overlying podzols, there are land depressions where sandy chernozem soils with very thick humus horizons dominate. In the past, they were the bottoms of fish breeding ponds, and currently they are directly adjacent to ponds and therefore constantly exposed to pond waters. In many respects, the Barycz Valley is a unique region. For one thing, it contains the highest number of fish ponds in Poland. Secondly, it is free from heavy industry and large cities. Thus, this region may be considered considerably clean, and the observed concentrations of trace elements are typical for non-degraded environments. There is, however, a threat of excessive accumulation of trace elements such as Zn, Pb and Cu in waters of the rivers in the Barycz drainage basin, received from point sources, and especially supplied with wastewater. These rivers play a very important role; namely, they are the source of water for filling up numerous ponds (Marek 1989). On the other hand, any seepage of river waters into the groundwater may cause excessive concentrations of trace elements in soils near the ponds.

The objective of the study was to analyse and assess sorption properties of sandy soils used as hay meadows. As the study was conducted in a special bird protection area (SBP) included in the European Ecological Network

Nature 2000, special attention was paid to the content of selected trace elements.

MATERIAL AND METHODS

The study was conducted on 6 soil profiles situated in the Barycz Valley, within a special bird protection area (SBP). According to the World Soil Resources classification (WRB 2006), the analysed soils may be rated as Mollic Gleysols (Arenic), Mollic Phaeozems (Arenic) and Endogenic Phaeozems (Arenic). Having identified and described their morphology, soil samples were collected from genetic horizons and the following analyses were conducted: particle size distribution using the Bouyoucos aerometric method modified by Casagrande and Prószyński, total organic carbon (TOC) using the Tiurin's oxidometric method, pH in H_2O and 1mol KCl dm^{-3} using the potentiometric method, the $CaCO_3$ dm^{-3} content using the Scheibler's method, exchange acidity (Ea) using the Sokołow's method, total N (Nt) content using the Kjeldahl's method, exchangeable base cations (Ca^{+2}, Mg^{+2}, K^+, Na^+) in an extract of 1mol CH_3COONH_4 dm^{-3} of pH 7 using the Pallman's method, and total content of the metals Fe, Mn, Zn, Pb and Cu dissolved in 70% $HClO_4$ and determined using the ASA method. The results of the study were elaborated statistically using correlation coefficients at significance levels of $p = 0.05$ and $p = 0.01$ with Statistica 9 software. An assessment of the degree of contamination with metals was performed according to the Regulation of the Ministry of the Environment of 2002, on standards on soil quality and standards of earth quality (Journal of Law no 165, item 1358 and 1359).

RESULTS AND DISCUSSION

Surface humus horizons A, marked as A1 horizons of the thickness of 6-11 cm, were distinguished in the morphological structure of the analysed soil profiles. Deeper lying humus horizons with visible gley or altered colour were marked as horizons A2 and A3 (Table 1). Humus horizons with transient horizons A/C reached the depth of 50 cm (profile no 1). The features of gley and traces of ferruginous and manganese participation in the form of stains, pimentos and vertical seepages were noted in most of the analysed soils. The gley contribution in particular soil profiles was differentiated and dependent on the intensity of reduction processes induced by the activity of stagnant groundwater lying at a depth from 28 cm (profile no 3 and 5) to 70 cm (profile no 2 and 6). The level of groundwater table determined the depth of soil sample collection for laboratory analysis.

Table 1

Grain size composition of soils according to the classification of PTG-2008 (2009)

Profile No.	Soil horizon	Depth (cm)	Skeletic parts	Sum of fraction			Texture classes according to USDA (2009)
			(%) content of fraction ∅ in mm				
			> 2.0	2.0 - 0.05	0.05 - 0.002	< 0.002	
Endogenic Phaeozems (Arenic)							
1	A1	0-10	0	90	9	1	sand
	A2	10-20	0	88	11	1	sand
	A3	20-34	0	89	9	2	sand
	A/Cgg	34-50	0	91	7	2	sand
	Cgg	>50	0	98	1	1	sand
Mollic Phaeozems (Arenic)							
2	A1	0-10	0	84	11	5	loamy sand
	A/C	10-30	1	79	12	9	loamy sand
	C	30-50	2	49	21	30	sandy clay loam
	IIC	50-70	1	97	1	2	sand
	IIIC	>70	0	99	0	1	sand
Mollic Gleysols (Arenic)							
3	A1	0-11	0	90	10	0	sand
	A2	11-17	0	82	18	0	loamy sand
	A3gg	17-28	0	93	6	1	sand
	Cgg	>28	0	92	7	1	sand
Mollic Gleysols (Arenic)							
4	A1	0-10	0	81	19	0	loamy sand
	A2	10-22	0	75	25	0	sandy loam
	A3gg	22-32	0	60	38	2	sandy loam
	A/Cgg	32-38	0	61	36	3	sandy loam
	Cgg	>38	0	86	9	5	sand
Mollic Gleysols (Arenic)							
5	A1	0-6	0	84	16	0	loamy sand
	A2	6-18	0	81	19	0	loamy sand
	A/Cgg	18-28	0	76	23	1	loamy sand
	Cgg	>28	0	69	29	2	loamy sand
Mollic Gleysols (Arenic)							
6	A1	0-10	0	85	14	1	sand
	A2gg	10-20	0	81	16	3	loamy sand
	A/Gox	20-45	0	79	13	8	loamy sand
	Goxr	45-70	0	91	3	6	sand
	Gr	>70	0	84	10	6	loamy sand

In sandy soils, the particle size distribution, excluding organic matter content, strongly determines the range of physical and physicochemical features (DROZD, LICZNAR 1996). In earthy parts of the analysed soil profiles, the sand fraction had the highest contribution (2-0.05 mm) and its content was at a level of 49 to 99%. The content of the silt fraction (0.05-0.002 mm) was considerably lower, usually less than 38%. A very small contribution of clay fraction (<0.002 mm), in the range of 1 to 30%, was observed in the

Table 2

Chemical properties of the soils

Profile No.	Soil horizon	Depth (cm)	pH		TOC	TN	TOC/TN
			H_2O	KCl	(g kg^{-1} soil)		
Endogenic Phaeozems (Arenic)							
1	A1	0-10	4.31	3.41	40.52	2.85	14.22
	A2	10-20	5.53	4.32	5.77	0.68	8.49
	A3	20-34	5.14	4.14	5.46	0.55	9.92
	A/Cgg	34-50	6.26	5.43	2.90	0.33	8.78
	Cgg	>50	6.53	6.04	1.50	n.d.	n.d.
Mollic Phaeozems (Arenic)							
2	A1	1-10	6.05	5.37	36.13	3.90	9.26
	A/C	10-30	6.42	5.53	22.09	2.40	9.20
	C	30-50	7.34	5.82	3.20	n.d.	n.d.
	IIC	50 -70	7.91	6.66	2.90	n.d.	n.d.
	IIIC	>70	7.14	6.44	2.70	n.d.	n.d.
Mollic Gleysols (Arenic)							
3	A1	0-11	5.23	4.32	34.14	3.10	11.01
	A2	11-17	4.71	3.84	62.11	4.40	14.12
	A3gg	17-28	5.03	4.27	20.29	1.00	20.29
	Cgg	>28	5.75	4.71	0.50	n.d.	n.d.
Mollic Gleysols (Arenic)							
4	A1	0-10	4.65	3.83	103.45	6.10	16.96
	A2	10-22	4.51	4.02	124.89	8.70	14.36
	A3gg	22-32	4.84	3.86	99.61	6.10	16.33
	A/Cgg	32-38	4.53	3.72	61.40	2.80	21.93
	Cgg	>38	5.22	4.21	6.40	n.d.	n.d.
Mollic Gleysols (Arenic)							
5	A1	0-6	4.42	3.63	79.72	5.60	14.24
	A2	6-18	4.38	3.66	85.50	5.40	15.84
	A/Cgg	18-28	4.52	3.71	50.67	6.70	7.56
	Cgg	>28	4.86	3.94	4.70	n.d.	n.d.
Mollic Gleysols (Arenic)							
6	A1	0-10	6.71	6.27	29.91	3.19	9.38
	A2gg	10-20	6.83	6.19	19.36	2.22	8.72
	A/Gox	20-45	6.95	6.32	4.12	0.57	7.23
	Goxr	45-70	7.34	6.43	0.89	n.d.	n.d.
	Gr	>70	7.52	6.38	0.50	n.d.	n.d.

Key: n.d. – not determined

samples (Table 1). Wide ranges of particular texture fractions prove the genetic diversity of particular soil horizons. The particle size distribution typical for loose sands, slightly loamy sands and loamy sands predominated in the examined soils (USDA 2009). In terms of soil heaviness, the examined soil profiles may be classified as very light and light.

Table 3

Coefficient of correlations between selected properties of soils

Variable	Fe (g kg^{-1})	Mn	Zn	Pb	Cu
		(mg kg^{-1})			
2.0-0.05 mm	-0.57**	-0.08	-0.11	-0.63**	-0.02
0.05-0.002 mm	0.19	-0.02	-0.06	0.65**	-0.03
<0.002 mm	0.84**	0.19	0.32	0.19	0.10
Depht (cm)	-0.01	-0.21	-0.11	-0.50**	0.01
pH KCl	0.40*	0.46*	0.16	-0.57**	0.10
TOC (g kg^{-1} soil)	-0.12	-0.18	-0.07	0.71**	-0.03
TN (g kg^{-1} soil)	-0.07	-0.06	-0.04	0.69**	-0.02
Ea (cmol(+) kg^{-1})	-0.10	-0.33	0.02	0.59**	0.08
S (cmol(+) kg^{-1})	0.74**	0.53**	0.41*	0.49**	0.22
CEC (cmol(+) kg^{-1})	0.67**	0.41*	0.38*	0.62**	0.23
BS (%)	0.44*	0.46*	0.17	-0.11	0.07

Statistically significant at $p < 0.05$*, $p < 0.01$**, $n = 28$.

The above soils were formed from carbonate-free formations, which was certainly conditioned by their sandy texture composition (Table 2). The values for pH in 1 mol KCl dm^{-3} were in the range of 3.41-6.66, indicating strongly acidic to neutral reaction. Also, the tendency for an increase in pH values in deeper genetic horizons was observed and confirmed statistically (Table 3). The pH values demonstrated, a significant positive relationship with the degree of the sorption complex saturation with base cations (BS), and negative relationships with the 0.05-0.002 mm fraction, exchange acidity (Ea), and the content of TOC and TN.

The humus horizons A were characterised by differentiated content of TOC (5.46-124.89 g kg^{-1}) and TN (0.55-8.70 g kg^{-1}), which distinctly decreased in deeper soil horizons (Table 2). A higher content of TOC and TN was determined in samples more abundant in the silt fraction (0.05-0.002 mm) and characterised by higher value of exchange acidity (Ea) and cation exchange capacity (CEC) – Table 4. The value of TOC/TN was in the range from 7.23 to 21.93, with some increasing tendency in deeper horizons.

Regarding the above properties, the analysed soils are similar to chernozems formed from sands found on the Tarnobrzeska plain and studied by Klimowicz (1980), ground-gley soils discussed by Giedrojć et al. (1990, 1992), chernozems and ground-gley soils of the Kampinos Forest analysed by Konecka-Betley et al. (1999), chernozems of the Poznańskie Lake District analysed by Marcinek and Komisarek (2004), soils of the Milicko-Głogowskie Depression (Łabaz et al. 2010*a*), soils of the Barycz Valley Landscape Park (Bogacz et al. 2008, Łabaz et al. 2008, 2010*b*, 2011) and chernozems of the Milicz area examined by Bogacz et al. (2010).

Table 4

Coefficient of correlations between selected soil properties

Variable	pH KCl	TOC ($g\ kg^{-1}$)	TN ($g\ kg^{-1}$)	Ea (cmol(+) kg^{-1})	S (cmol(+) kg^{-1})	CEC (cmol(+) kg^{-1})	BS (%)
2.0-0.05 mm	0.27	-0.37	-0.32	-0.42	-0.55**	-0.63**	0.02
0.05-0.002 mm	-0.54**	0.63**	0.58**	0.62**	0.42*	0.55**	-0.23
<0.002 mm	0.38*	-0.33	-0.33	-0.21	0.41*	0.33	0.35
Depth (cm)	0.60**	-0.59**	-0.66**	-0.56**	-0.37	-0.49**	0.36
pH KCl	-	-0.63**	-0.56**	-0.76**	0.16	-0.05	0.72**
TOC ($g\ kg^{-1}$)	-0.63**	-	0.94**	0.64**	0.37	0.51**	-0.17
TN ($g\ kg^{-1}$)	-0.57**	0.94**	-	0.63**	0.44*	0.58**	0.15
Ea (cmol(+) kg^{-1})	-0.76**	0.64**	0.63**	-	0.11	0.37	-0.72**
S (cmol(+) kg^{-1})	0.16	0.37	0.44*	0.11	-	0.97**	0.46*
CEC (cmol(+) kg^{-1})	-0.05	0.51**	0.58**	0.37	0.97**	-	0.24
BS (%)	0.72**	-0.17	-0.15	-0.72**	0.46*	0.24	-

Statistically significant at $p < 0.05$*, $p < 0.01$**, $n = 28$

Magnesium, calcium, potassium and sodium are present in soil in various forms, of which their exchangeable forms are the most important for plant nutrition. Cations adsorbed on soil colloids are a specific pool of nutrients (Kobierski et al. 2011). In arable soils, the sorption properties depend mainly on their particle size distribution, organic matter content and applied fertilization (Askegaard et al. 2005, Ersahin et al. 2006).

The sorption complex of the analysed soils was highly saturated with base cations, mostly calcium, followed by magnesium (Table 5). The contribution of other cations, e.g. potassium and sodium, was often in the range of trace amounts. Both the content and distribution of exchange base cations of in particular profiles of the examined soils were strongly differentiated and strictly connected to the content of particular particle size fractions, which was confirmed by the calculated correlation coefficients (Table 4). Higher sums of base cations (S) and cation exchange capacity (CEC) were noted in samples characterised by higher contributions of silt and clay fractions. This relationship was also confirmed in earlier studies by Błaszczyk (1998) and Kobierski et al. (2011). The exchange acidity was in the range of 0.11 to 5.15 cmol(+) kg^{-1}, and its value decreased significantly in deeper genetic horizons (Table 5). The Ea values demonstrated a positive relationship with the content of the silt fraction, TOC and TN, while having a significant, negative relationship with the degree of sorption complex saturation (BS) – Table 4. The sum of exchangeable base cations (S) ranged from 1.19 to 19.74 cmol(+) kg^{-1}, while the cation exchange capacity (CEC) was within the range of 1.57 to 23.20 cmol(+) kg^{-1}. The degree of the saturation of the sorption complex with base cations (BS), following a wide range of the results on sorption

Table 5

Sorption properties of the soils

Profile No.	Soil horizon	Depth (cm)	Ca^{+2}	Mg^{+2}	K^{+}	Na^{+}	Ea*	S**	CEC***	BS****
			(cmol(+) kg^{-1})							(%)
Endogenic Phaeozems (Arenic)										
1	A1	0-10	1.20	1.14	0.31	0.18	5.15	2.83	7.98	35.5
	A2	10-20	1.14	0.48	0.05	0.15	3.43	1.82	5.25	34.7
	A3	20-34	1.50	0.46	0.06	0.13	1.31	2.15	3.46	62.1
	A/Cgg	34-50	2.00	0.50	0.02	0.14	0.61	2.66	3.27	81.3
	Cgg	>50	1.46	0.02	0.02	0.13	0.21	1.63	1.84	88.6
Mollic Phaeozems (Arenic)										
2	A1	1-10	16.80	2.10	0.20	0.50	3.60	19.60	23.20	84.5
	A/C	10-30	17.60	1.20	0.10	0.50	3.00	19.40	22.40	86.6
	C	30-50	16.80	1.50	0.20	0.60	1.00	19.10	20.10	95.0
	IIC	50-70	2.40	0.40	0.10	0.30	0.50	3.20	3.70	86.5
	IIIC	>70	1.20	0.20	0.10	0.20	0.50	1.70	2.20	77.3
Mollic Gleysols (Arenic)										
3	A1	0-11	5.12	0.68	0.11	0.17	1.14	6.08	7.22	84.2
	A2	11-17	7.36	0.58	0.12	0.18	2.54	8.24	10.78	76.4
	A3gg	17-28	3.04	0.34	0.05	0.14	0.82	3.57	4.39	81.3
	Cgg	>28	0.80	0.28	0.03	0.08	0.38	1.19	1.57	75.8
Mollic Gleysols (Arenic)										
4	A1	0-10	8.40	1.26	0.18	0.29	3.19	10.13	13.32	76.1
	A2	10-22	14.00	1.61	0.19	0.38	2.15	16.18	18.33	88.3
	A3gg	22-32	12.00	1.65	0.11	0.38	4.95	14.14	19.09	74.1
	A/Cgg	32-38	6.64	1.16	0.07	0.26	4.22	8.13	12.35	65.8
	Cgg	>38	2.40	0.56	0.05	0.14	0.98	3.15	4.13	76.3
Mollic Gleysols (Arenic)										
5	A1	0-6	5.76	0.98	0.27	0.31	4.03	7.32	11.35	64.5
	A2	6-18	5.12	0.76	0.19	0.29	5.04	6.36	11.40	55.8
	A/Cgg	18-28	5.14	0.60	0.09	0.19	4.22	6.02	10.24	58.8
	Cgg	>28	2.40	0.44	0.05	0.14	3.47	3.03	6.50	46.6
Mollic Gleysols (Arenic)										
6	A1	0-10	16.80	2.24	0.21	0.49	0.11	19.74	19.85	99.4
	A2gg	10-20	14.40	1.00	0.06	0.31	0.05	15.77	15.82	99.7
	A/Gox	20-45	8.40	0.78	0.05	0.27	0.61	9.50	10.11	94.0
	Goxr	45-70	4.01	0.54	0.04	0.17	0.11	4.76	4.87	97.7
	Gr	>70	3.60	0.56	0.04	0.17	0.11	4.37	4.48	97.5

* Exchangeable acidity; ** Sum of exchangeable cations; *** Cation exchange capacity; **** Base saturation

properties, was within 34.7 to 99.7%. Both the sum of base cations (S) and cation exchange capacity (CEC) demonstrated lower values in samples more abundant in the sand fraction. Moreover, the cation exchange capacity (CEC) demonstrated higher values in samples more abundant in the silt fraction, TOCorg and TN, which was confirmed statistically.

Table 6

Content of Fe and trace elements in the soils

Profile No.	Soil horizon	Depth (cm)	Fe	Mn	Zn	Pb	Cu
			(g kg-1)	(mg kg-1)			
Endogenic Phaeozems (Arenic)							
1	A1	0-10	1.97	93.63	66.00	5.83	4.39
	A2	10-20	1.86	99.82	42.53	5.83	17.48
	A3	20-34	1.87	76.58	30.46	2.66	24.00
	A/Cgg	34-50	1.62	42.81	22.03	1.00	57.72
	Cgg	>50	2.78	36.67	10.64	1.45	37.65
Mollic Phaeozems (Arenic)							
2	A1	1-10	26.10	293.68	64.55	22.71	44.41
	A/C	10-30	23.60	294.93	42.59	31.17	32.73
	C	30-50	51.40	232.11	47.03	38.33	15.38
	IIC	50-70	4.70	42.68	8.20	4.20	2.80
	IIIC	>70	1.70	28.37	5.30	4.10	3.70
Mollic Gleysols (Arenic)							
3	A1	0-11	3.90	352.28	21.84	26.52	5.70
	A2	11-17	2.30	48.54	11.13	29.04	2.20
	A3gg	17-28	1.40	50.66	7.10	18.02	1.30
	Cgg	>28	0.80	21.83	3.00	11.00	0.50
Mollic Gleysols (Arenic)							
4	A1	0-10	5.50	36.76	18.14	30.03	10.11
	A2	10-22	5.90	36.34	20.23	32.67	13.53
	A3gg	22-32	8.60	41.90	17.56	31.52	24.63
	A/Cgg	32-38	8.40	46.77	12.93	26.04	14.56
	Cgg	>38	2.60	28.56	5.70	14.45	1.10
Mollic Gleysols (Arenic)							
5	A1	0-6	4.70	62.73	14.54	36.53	5.50
	A2	6-18	5.50	49.80	17.63	33.46	5.70
	A/Cgg	18-28	4.40	39.88	11.24	26.04	3.30
	Cgg	>28	4.20	37.72	8.48	18.02	0.60
Mollic Gleysols (Arenic)							
6	A1	0-10	16.70	815.32	20.22	6.67	4.90
	A2gg	10-20	19.10	923.75	17.30	5.67	4.10
	A/Gox	20-45	30.70	930.09	10.18	4.00	2.59
	Goxr	45-70	7.63	114.38	3.65	2.00	1.40
	Gr	>70	3.86	61.52	7.23	1.50	2.18

The levels of iron (Fe) and manganese (Mn) in the examined soil depended above all on the changing red-ox conditions, especially in profiles with high levels of groundwater. Both elements very easily undergo oxidation and reduction processes, which results in their increased solubility and mobility (ORZECHOWSKI, SMÓLCZYŃSKI 2010). The content of Fe was in the range of 0.80 to 51.40 g kg^{-1}, while the Mn amounts varied from 21.83-930.09 g kg^{-1} (Table 6). Both elements were significantly positively

Table 7

Coefficient of correlations between selected trace elements

Variable	Fe	Mn	Zn	Pb
Fe	-	0.57**	0.42*	0.27
Mn	0.57**	-	0.08	-0.20
Zn	0.42*	0.08	-	0.10
Pb	0.27	-0.20	0.10	-
Cu	0.16	-0.10	0.91**	-0.02

Statistically significant at $p < 0.05$*, $p < 0.01$**, $n = 28$

correlated with each other and with the pH and sorption properties (Tables 3 and 7). Iron (Fe) additionally demonstrated a strong positive relationship with the clay fraction and a strong negative relationship with the sand fraction (Table 3). The determined amounts of Fe and Mn and their relationships with soil texture and sorption properties were similar to the results obtained by KONECKA-BETLEY et al. (1996, 1999), ORZECHOWSKI and SMÓLCZYŃSKI (2010), ŁABAZ et al. (2011).

The other examined elements, i.e. Zn, Pb and Cu, were observed in considerably smaller amounts than Fe and Mn. The zinc (Zn) content was in the range of 3.00 to 66.00 mg kg^{-1}, lead (Pb) from 1.00 to 38.33 mg kg^{-1}, and copper (Cu) from 0.50 to 44.41 mg kg^{-1} (Table 6). The decreasing tendency in the Zn, Pb and Cu content in deeper genetic horizons appeared in all the examined soil profiles, although was confirmed statistically only in the case of Pb (Table 3). The determined amounts of Zn were very similar to the data presented by ANDRUSZCZAK and CZUBA (1984), who assessed the Zn content in Polish chernozems on a level of 13-150 mg kg^{-1}. Zinc had significant positive correlations with the sum of base cations (S) and cation exchange capacity (CEC), as well as with the Fe and Cu content. Total Zn content was the highest in humus horizons and was subject to a decrease in deeper situated genetic horizons. This is probably caused by biological accumulation in humus horizons which was observed previously in the study by DOMAŃSKA (2009). The Pb content was close to the one observed in mucky chernozems and ground-gley soils in the Kampinos Forest area (KONECKA-BETLEY et al. 1996, 1999). In our research, the lead content was found in the highest number of significant correlations with the examined soil parameters, namely it was positively correlated with the silt fraction, TOC, TN, S, CEC, while negatively correlated with an increasing depth of the soil profile, sand fraction and pH value. The total Cu content was similar to that found by KABATA-PENDIAS (1981) and ANDRUSZCZAK and CZUBA (1984) in Polish chernozems and in ground-gley soils of the Kampinos Forest, but higher when compared to the results in degraded and mucky chernozems in the same area (KONECKA-BETLEY et al. 1996, 1999). Copper (Cu), except for the strong positive relationship with zinc (Zn), did not demonstrate any significant correlations with the analysed parameters of the soils.

Our assessment of the degree of heavy metal contamination in the examined soils, referred to to the Regulation of the Ministry of the Environment on standards on soil quality and standards of earth quality (Journal of Law no 165, item 1358 and 1359), showed to excess of the permissible levels of Zn, Pb and Cu.

CONCLUSIONS

1. The genesis of the examined soils can be linked to the very wet environs, which significantly manner influenced their physical and physicochemical parameters. These soils were formed in an area dominated by breeding fish ponds and crisscrossed with a dense network of watercourses in the Barycz River drainage basin.

2. The sum of base exchange cations (S) and the cation exchange capacity (CEC) in the examined soils are strongly connected to the particle size distribution, the finding confirmed by significant positive relationships with the silt fraction and colloidal fraction, and significant negative correlations with the sand fraction.

3. Higher content of Zn, Pb and Cu in surface genetic horizons of the examined soil profiles may point to their anthropogenic origins. The examined soils, apart from the dominant sandy texture, are characterised by a thick humus horizon abundant in TOC and TN, which increases soil capacity for trace elements accumulation.

4. Our assessment of the contamination of the soils with respect to the content of Zn, Pb and Cu does not demonstrate any excess of the permissible levels of these trace elements.

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