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Variability of morphological, physical and chemical properties of soils derived from carbonate-rich parent material in the Pieniny Mountains (south Poland)

Abstract: Carbonate-rich soils are characterized by great diversity in content of carbonate and non-carbonate mineral substances in soil substrate which largely influences soil properties. The study presents the analysis results of four soil profiles located at the area of Pieniny National Park. The aim of this study was to characterize and classify the soils developed from the mixture of carbonate and carbonate-rich rock material, formerly classified as pararendzinas. It was achieved by determination of morphological, physical, and chemical properties, as well as mineralogical composition of selected carbonate-rich soils occurring in the Polish part of the Pieniny Mts. Soils were classified as typical chernozemic rendzina (P1), typical eutrophic brown soils (P2, P4), as well as typical pararendzina (P3) according to Polish Soil Classification (2011).

The parent material of studied soils P1, P2 and P4 were slope covers, with a dominant share of sandstone and minor share of limestone, whereas soil P3 was formed from variegated shale cut with multiple calcite veins. Soils were characterized by stable aggregate structure: crumby, angular blocky and subangular blocky. They were medium or strong skeletal, mostly with loam texture with great share of silt fraction. $CaCO_3$ content in genetic horizons ranged from 0.0 to 703.0 g·kg^{-1}. The reaction of studied soils was from weakly acidic to alkaline. Analysed soils were characterized by very high base saturation. Among determined exchangeable cations, Ca^{2+} ions had the biggest share in all analysed profile. High base saturation, as well as high content of calcium carbonate was accompanied by content of organic matter and percentage content of clay fraction. Taking into consideration determined chemical and physical properties, it can be found that investigated soils were influenced by not only the *in-situ* weathering material but also by rock material which have been transported and deposited as a result of slope processes. Furthermore, the lack or lower content of $CaCO_3$ in surface and middle part of analysed soil profiles was most likely a result of the impoverishment of rock material during the transport on the slope.

Keywords: carbonate-rich soils, Carpathian's soils, Phaeozems, Cambisols, Regosols

INTRODUCTION

Diversification of soil cover at the area of the Pieniny Mts. is conditioned by variability of geological substrate and morphology of the terrain (Niemyska-Łukaszuk et al. 2002, Skiba et al. 2002, Zaleski et al. 2006). The most frequently occurring carbonate rocks in the area of Pieniny National Park (PNP) include (1) limestone and marl, which are parent rock of rendzinas, (2) clastic rocks with a high carbonate content mixed with fragments of limestone, from which pararendzinas are form, as well as (3) sandstone and shale that has an insignificant admixture of carbonate cement, from which soils with *cambic* horizons are formed (Niemyska-Łukaszuk et al. 2002, 2004). Carbonate-rich soils are characterized by specific calcium-silicate soil substrate which largely influences soil properties (Zagórski 2001). Percentage share of the areas of individual soil taxonomic units within PNP are determined by the lithogenic relations. Carbonate-rich soils characterized by different degrees of development occupy 60% of the PNP area (Niemyska-Łukaszuk et al. 2002, 2004).

Formerly in Pieniny Mts. area, all soils developed on rocks enriched in carbonates as well as soils formed on slope covers containing mixture of weathered carbonate and non-carbonate rocks were classified as pararendzinas (Adamczyk et al. 1980). In a wider range pararendzinas were studied by Zasoński (1981, 1992, 1993, 1995a, 1995b), who described pararendzinas from area of Eastern Carpathians, Cieszyn area and Rymanów Hills (Table 1). Furthermore, Niemyska-Łukaszuk et al. (2002, 2004, 2010) described pararendzinas at the area of Babia Góra National Park and PNP (Table 1). Pararendzinas at the area of Pieniny were described also by Kacprzak and Żyła (2006) (Table 1). Moreover, individual profiles of pararendzinas at the area of Częstochowa Upland, Masurian Lake District, Nałęczów Plateau, Góra Zborów Nature Reserve and others were described (Kobylecka 1981, Lemkowska and Sowiński 2008, Paluszek 2010, Fajer and Waga 2012) (Table 1). Large part of these soils,

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TABLE 1. Bibliography of pararendzinas' research in Poland

Author(s)	Location	Soil type	Translation proposed by authors	Parent material
Zasoński and Skiba 1988	Cieszyn area, Western Carphatians	pararędzina właściwa, pararędzina brunatna (PTG 1989)	proper pararendzina, brown pararendzina	shale, marl, sandstone
Kobylecka 1981	Kraków-Częstochowa Upland, S Poland	pararędzina czarnoziemna (PTG 1974)	chermozem pararendzina	limestone and marl
Zasoński 1992	Miejsce Piastowe and Rymanów, Eastern Carpathians	pararędzina właściwa, pararędzina brunatna (PTG 1989)	proper pararendzina, brown pararendzina	sandstone and shale
Zasoński 1993	Eastern Carpathians	pararędzina inicjalna, pararędzina właściwa, pararędzina brunatna (PTG 1989)	initial pararendzina, proper pararendzina, brown pararendzina	sandstone and shale
Zasoński 1995a	Eastern Carpathians	pararędzina inicjalna, pararędzina właściwa (PTG 1989)	initial pararendzina, proper pararendzina	sandstone, shale and limestone
Zasoński 1995b	Eastern Carpathians	pararędzina brunatna (PTG 1989)	brown pararendzina	shale, calcite-bearing sandstone
Niemyska-Łukaszuk et al. 2002	Pieniny National Park	pararędzina brunatna, pararędzina czarnoziemna (PTG 1989)	brown pararendzina, chermozem pararendzina	sandstone and shale
Kacprzak and Żyła 2006	Lesser Pieniny	pararędzina brunatna (PTG 1989)	brown pararendzina	marl and limestone
Kacprzak et al. 2006	Szopczański Gorge, Pieniny National Park	pararędzina brunatna (PTG 1989)	brown pararendzina	limestone and sandstone
Lemkowska and Sowiński 2008	Masurian Lake District, NE Poland	pararędzina właściwa (PTG 1989)	proper pararendzina	glacial sediments
Łuszczyński and Łuszczyńska 2009	Nida Basin, central Poland	pararędzina właściwa (PTG 1989)	proper pararendzina	limestone, marl and loess
Paluszek 2010	Nałęczów Plateau, Lublin Upland, SE Poland	pararędzina inicjalna (PTG 1989)	initial pararendzina	glacial sediments – till and sand
Sowiński and Lemkowska 2010	Olsztyn Lake District, NE Poland	pararędzina właściwa (PTG 1989)	proper pararendzina	calcareous gyttja, calcareous clay gyttja
Rybicki 2010	Kielce Upland, central Poland	pararędzina inicjalna (PTG 1989)	initial pararendzina	siltic sediment
Krysiak et al. 2010	Radomszczańskie Hills, Małopolska Upland, S Poland	pararędzina brunatna (PTG 1989)	brown pararendzina	limestone, marly limestone, quaternary sand, glacial till,
Niemyska-Łukaszuk et al. 2010	Babia Góra National Park	pararędzina właściwa (PTG 1989)	proper pararendzina	shale
Fajer and Waga 2012	Góra Zborów Nature Reserve, Kraków-Częstochowa Upland, S Poland	pararędzina z cechami brunatnienia (PTG 2011)	brown pararendzinas	fine-grain sediments (sand and silt) with weathering products of limeston
Lasota et al. 2014	Grabowiec Nature Reserve, N Poland	pararędzina właściwa (PTG 1989)	proper pararendzina	sandstone and shale

despite the fact, that they have been earlier classified as pararendzinas, currently would not comply with all diagnostic criteria for these soils according to PSC (2011).

The subsequent editions of Polish Soil Classification (PSC) distinguishes pararendzinas as soils formed from clastic rocks that are rich in calcium carbonate (A Natural and Genetical Classification of Polish Soil 1956, Genetical Classification of Polish Soil 1959, PSC 1974, 1989, 2011). The similar soil taxonomic units occur in German soil classification (Arbeitskreis für Bodensystematik der Deutschen Bodenkundlichen

Gesellschaft 1998), however pararendzinas are not distinguished in international classification such as Soil Taxonomy (1999) and World Reference Base for Soil Description (IUSS Working Group WRB 2015). In the current edition of PSC (2011), pararendzinas occur in the order of weakly developed soil, within which typical pararendzinas and brown pararendzinas are distinguished. According to PSC (2011), pararendzinas are soils which contain at least 15% calcium carbonate in parent material and they are characterized by neutral or alkaline reaction (pH ranging from 6.0 to 7.5).

Referring to other authors, typical pararendzinas can be classified according to IUSS Working GroupWRB (2015) as Lithic Leptosols, Calcaric-Lithic Leptosols, Haplic Regosol (Calcaric) Haplic Calcisols (Niemyska-Łukaszuk et al. 2002, 2004; PSC 2011), whereas brown pararendzinas are classified as Calcaric Cambisols, Skeletic-Calcaric Cambisols, Haplic Regosol (Calcaric), Cambic Calcisols, Calcaric Calcisols (Skiba et al. 2002, Niemyska-Łukaszuk et al. 2002, 2004, PSC 2011).

In general, carbonate-rich soils in the Carpathian Mountains occur at small areas in the complexes with Cambisols, what is the result of spatial variability of the parent rock (Zasoński 1993, 1995a, 1995b). Formation of carbonate-rich soils accompany significant predominance of lithological features over pedogenic features. Those soils are often found in locations of landslides exposures (Zasoński 1995a). Due to the high content of rock fragments, loamy texture (e.g. sandy loam, loam, silty clay loam), as well as shallow soil profile, carbonate-rich soils are not suitable for agricultural use. Furthermore, carbonate-rich soils s are frequently covered by deciduous forests. Xerothermic plant communities appearing on the rocks can be also found in places where those soils occur (Zasoński 1993, Krysiak et al. 2010, Fajer and Waga 2012).

According to Zasoński (1992), pararendzinas should differ from rendzinas what is manifested by varied carbonate content in parent material and the difference in the intensity of weathering or smaller share of carbonate debris in the soil profile (Zasoński 1993, 1995b). Pararendzinas can evolve into brown earth soils (Zasoński 1992), in particular due to advanced decalcitization process of the parent material (Zasoński 1995b). Nevertheless, pararendzinas and rendzinas in the mountain areas are similar in terms of their physical properties, e.g. grain size distribution, content of rock fragments, durability of aggregates and water retention (Niemyska-Łukaszuk 2002, Zaleski et al. 2006).

Carbonate-rich soils can have well-developed humus horizon, which is characterized by crumby structure (Zasoński 1992, Zaleski et al. 2016). Depending on the parent rock, from which carbonate-rich soils have evolved, organic matter can occur within the soil profile (Krysiak et al. 2010, Fajer and Waga 2012). The presence of organic matter within the soil profile is characteristic especially in case when varied flysch subfacies constitute parent material (Zasoński and Skiba 1988, Zasoński 1992).

The analysis of the chemical composition of carbonate-rich soils provides an information, which is helpful to soil processes interpretation (Kacprzak et al. 2006). Within the carbonate-rich soils, depending of the parent rock, the calcium carbonate content can increase with depth. In some cases, decalcification in the middle part of soil profile can occur (Zasoński and Skiba 1988, Zasoński 1992, Zasoński 1993). Moreover, the soils are characterized by high sorption capacity (Niemyska- Łukaszuk et al. 2004, Zaleski et al. 2016).

Nowadays, within the researches over carbonate-rich soils, not many of them is focusing on pararendzinas, especially with respect to difficulties connecting with their classification. Moreover, changes in the criteria for pararendzinas classification, implemented with the update of PSC (2011), were the basis for conducting the studies over that soils occuring in the Pieniny Mts. The aim of this study was to characterize and classify the soils developed from the mixture of carbonate and carbonate-rich rock material, occurring in the Polish part of the Pieniny Mts., formerly classified as pararendzinas.

MATERIALS AND METHODS

Four soil profiles from area of PNP were investigated. Profile P1 was sampled in Tylka village, profiles P2 and P4 in Sromowce Niżne village, and profile P3 in Hałuszowa village. Colluvial material containing sandstone and smaller amounts of limestone fragments were parent materials of P1, P2 and P4 soils profile. The parent material of profile P3 was variegated shale cut by calcite veins (Table 2).

To identify the main mineral phases, X-ray powder diffraction analysis were performed. It was accomplished on the air-dry smaller than 2,0 mm particles of soil samples using a Philips X'Pert APD diffractometer (Cu-Kα radiation generated at 40 kV and 30 mA by generator PW 1870, and equipped with vertical goniometer PW 3020) at the Institute of Geological Sciences, Jagiellonian University, Kraków, Poland. Mineralogical composition was determined only in selected horizons from profile P1, P2 and P3 (Fig.).

Soil samples underwent determination of basic physical and chemical properties. Color according to

TABLE 2. Location, morphological properties and texture of the studied soils

Profile No / GPS position/slope rating/exposure/ elevation a. s. l	Features of parent material	Depth (cm)	Soil horizon	Munsell's color	Structure	Rock fragments (mm) (%)	Particle-size (mm) distribution (%)			Texture (IUSS Working Group WRB 2015)
						>2.0	2.0–0.5	0.05–0.002	<0.002	
Typical chernozemic rendzina * Calcaric Skeletic Phaeozems (Colluvic, Loamic) Plant community **: *Dentario glandulosae-Fagetum typicum var. typicum*										
P1 49°25'26.6"N 20°29'08.5"E 12–15°N 664 m a. s. l.	limestone and sandstone colluvium, rubble	1–15	Ahca1***	10YR 2/3	s3gr	30	53	41	6	SL
		15–30	Ahca2***	10YR 3/3	s3gr	45	68	28	4	SL
		30–40	ACca***	10YR 4/2	d2os	40	41	45	14	L
		40–65	Cca1	10YR 5/4	d2os	40	48	32	20	SiL
		65–90	Cca2	10YR 7/3	d2os	80	29	53	18	SL
		90–120	Cca3	7.5YR 4/4	d2os	85	46	41	13	L
Typical eutrophic brown soil * Calcaric Skeletic Eutric Cambisols (Colluvic, Loamic) Plant community **: *Dentario glandulosae-Fagetum typicum var. typicum*										
P2 49°24'40.5"N 20°22'31.2"E 30° W 531 m a. s. l.	limestone and sandstone, occasionally red sandstone	0.5–22	Ah	10YR 4/2	s3gr	10–15	41	37	22	L
		22–33	AB	10YR 4/4	d3os	20	30	58	12	SL
		33–60	Bw	10YR 5/3	d3os	25	23	42	35	CL
		60–85	BC	10YR 5/4	d3os	60	26	49	25	L
		85–110	2Cca1	10YR 5/3	d1os	80	26	45	29	CL
		>110	2Cca2	2.5Y 4/2	d1os	90	28	45	27	SiCL
Typical pararendzina* Calcaric Skeletic Regosols (Loamic) Plant community **: *Dentario glandulosae-Fagetum typicum var. typicum*										
P3 49°25' 11.13"N 20°21' 47.59"E 3° SEE 680 m a. s. l.	varigated shale with interbeds of calcite veins	2–7	Ahca***	5YR 3/2	s3gr	5	13	57	30	SiCL
		7–20	Aca***	5YR 3/3	d3oa	10	7	57	36	SiCL
		20–33	Cca1	2.5Y 6/2	d3oa	65	24	46	30	CL
		33–50	Cca2	5YR 5/2	d2oa	50	21	49	30	CL
		50–90	Cca3	2.5Y 4/3	d2oa	40	21	54	25	SiL
Typical eutrophic brown soil Calcaric Skeletic Eutric Cambisols (Loamic) Plant community **: *Dentario glandulosae-Fagetum typicum var. typicu*m										
P4 49°25'05.9"N 20°20' 38.1"E 10° W 625 m a. s. l.	decalcified cover slope on carbonate rocks	0–2	Ah	10YR3/3	s3gr	0	16	51	33	SiCL
		2–10	A	10YR4/3	d3os/d3oa	20	25	40	35	CL
		10–35	AB	10YR5/4	d3os/d3oa	40	17	39	44	C
		35–60	BC	2.5Y4/3	s3os/s3oa	60	16	40	44	SiCL
		60–90	2Cca	2.5Y4/2	m	70	40	30	30	CL

Explanation: Textures: C – clay, CL – clay loam, L – loam, SL – sandy loam, SiCL – silty clay loam, SiL – silt loam; s3gr: medium crumby stable; d2os: fine blocky subangular semi-stable; d3os: fine blocky subangular stable; d1os: fine blocky subangular nonstable; d3oa: fine blocky angular stable; d1os: fine blocky angular nonstable; d2oa: fine blocky angular semistable; bd3os/bd3oa: very fine blocky subangular stable/ very fine blocky angular stable; s3os/s3oa: medium blocky subangular stable/ medium blocky angular stable; m: massive structure, *translation proposed by Świtoniak et al. (2016), ** according to Pancer-Kotej and Kaźmierczakowa (2004), ***Despite the criteria given by PSC 2011, authors decided to add the “ca” symbol due to large content of $CaCO_3$.

Munsell`s scale was defined with “Revised Standard Soil Color Charts” (Oyama and Takehara 1970). Particle-size distribution was determined by hydrometer-sieve method according to Polish Standard (1998). For the determination of pH values, a potentiometric method was employed. The pH was measured in H_2O and 1M KCl solution, in a ratio of 1:2.5 (w/v). Organic carbon content was determined using the potassium dichromate and Mohr’s salt, without the calcium carbonate removing (Lityński et al. 1976). Total nitrogen was measured using LECO®CNS 2000 apparatus at Department of Soil Science and Soil Protection, University of Agriculture, Kraków. Estimation of the $CaCO_3$ content was performed by treating the soil with hydrochloric acid (Lityński et al. 1976). Total potential acidity (TPA) were extracted in 0.5 M of sodium acetate at pH 8.2, while the sum of exchangeable bases (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were extracted in 1 M NH_4Cl at pH 7.0 (Kociałkowski et al. 1984) and analysed with ICP-OES Optima 7300 DV at Department of Agricultural and Environmental Chemistry, University of Agriculture, Kraków.

RESULTS

Investigated soils were located on hills with different slope inclination and with northern (P1), western (P2, P4) and south-eastern (P3) exposition (Table 2). Thicknesses of soils were diverse (Table 2). Soils, which were derived from colluvial material (P1, P2, P4) were thicker than soil developed directly on variegated shale (P3). Soil horizons in profiles P1, P2 and P4 were mainly yellow-brown to brown color. Soil from profile P3 was red-brown, which was caused by the primary red color of parent variegated shale (Table 2).

Topsoil horizons of all profiles consist of stable crumby aggregates. In the subsoil horizons, more or less stable, blocky angular and blocky subangular aggregates were present (Table 2).

Mineralogical compositions of soils horizons was similar in every analyzed sample (Fig.). Soil horizons contain quartz and calcite as the main phases. Small amounts of feldspars, micas and some clay minerals (1.47 and 0.71 nm peaks) were present. Proportion of quartz and calcite differs from sample (horizon) to sample.

The amount of gravel fragments usually was increasing with the depth of profile (Table 2), but amount of coarse fraction was often more than 10% even in the uppermost horizons (Table 2). Despite the various proportions of sand, silt and clay in the horizons, most of samples were classified as loam (Table 2). Commonly, the most abundant grain size fraction in analysed horizons were silt- and clay-size grains. In the humus horizon of profile P1, amount of sand was higher than the amount of silt and clay (Table 2).

Reaction of the soils was weakly acidic to neutral (pH in the range from 7.8 to 8.8 in H_2O and from 6.5 to 7.6 in KCl solution). In each profile, pH values (both in H_2O and KCl) increase with the depth (Table 3). The most acidic sample was soil P4, which does not contain any carbonates in the upper 60 cm of the profile.

Investigated soils were characterized by high concentration of total organic carbon (TOC) and total nitrogen (Table 3). In the topsoil horizons, TOC ranged from 44.9 to 89.0 $g{\cdot}kg^{-1}$ and N ranged from 3.7 to 5.6 $g{\cdot}kg^{-1}$. In the profiles P1, P2 and P3, TOC was present even in the deepest horizons. High values of C:N ratio in humus horizons (usually higher than 10) indicate maturity of organic matter. The highest values of C:N ratio was identified in profile P3 at the depth from 20 to 33 cm (Table 3).

In the deeper and middle parts of soils, concentration of $CaCO_3$ were noticeably higher than in humus horizons, with exception of P4, where carbonates occur only in parent material (Table 3, Fig.). The lowest content of $CaCO_3$ in parent material was indicated in profile P2 (173.0 $g{\cdot}kg^{-1}$), whereas the highest amount of $CaCO_3$ in profile P1 (703.0 $g{\cdot}kg^{-1}$) were found (Table 3).

Cation exchange capacity (CEC) of investigated soils was high, e.g. in case of profile P4, it reached 258.0 $mmol{\cdot}kg^{-1}$ in the humus horizon (Table 3). Soil sorption complex in all investigated profiles was mostly saturated by basic cations (Table 3), from which Ca^{2+} predominated. The ranged of Ca^{2+} cations was from 103.7 to 225.0 $mmol{\cdot}kg^{-1}$ (Table 3). Saturation of soil by Mg^{2+}, K^+ and Na^+ cations was much lower (Table 3). Total potential acidity (TPA) of soils was low and ranged from 1.1 to 13.4 $mmol{\cdot}kg^{-1}$ (Table 3). Usually, higher values of TPA were typical of topsoil horizons (Table 3). The sum of exchangeable bases was high (Table 3).

Based on the FAO-WRB (IUSS Working Group WRB 2015) classification, analyzed soils were classified as Calcaric Skeletic Phaeozems (Colluvic, Loamic) – soil P1; Calcaric Skeletic Eutric Cambisols (Colluvic, Loamic) – soil P2; Calcaric Skeletic Regosols (Loamic) – soil P3 and Calcaric Skeletic Eutric Cambisols (Loamic) – soil P4. According to PSC (2011) soil P1 was classified as typical chernozemic rendzina, soil P2 and P4 as typical eutrophic brown soils, whereas P3 was classified as typical pararendzina (Table 2). Taking into consideration the criteria given by third and fourth edition of PSC (1974, 1989) it should be mentioned that all studied soils supposed to be classified as pararendzinas.

TABLE 3. Chemical properties of the studied soils

Profile	Depth	Soil horizon	pH		TOC	N	C:N	$CaCO_3$	Ca^{2+}	Mg^{2+}	Na^+	K^+	TPA	TEB	ECEC	BS
	(cm)		H_2O	KCl	$(g\cdot kg^{-1})$			$(g\cdot kg^{-1})$	$mmol\cdot kg^{-1}$ of soil							%
P1	1–15	Ahca1	7.7	6.9	59.2	3.9	15.0	64.0	140.3	5.4	1.3	5.1	8.9	152.2	161.1	94.4
	15–30	Ahca2	7.9	7.2	26.7	1.7	15.5	148.0	106.5	14.1	1.5	5.8	7.1	127.8	135.0	94.5
	30–40	ACca	8.2	7.2	13.2	1.8	7.5	360.0	131.4	3.0	1.0	5.1	5.4	140.5	145.9	96.3
	40–65	Cca1	8.2	7.6	11.6	1.0	11.7	703.0	103.7	3.2	0.8	2.9	4.5	110.7	115.2	96.1
	65–90	Cca2	8.6	7.4	9.3	0.8	11.4	349.0	131.6	4.0	1.0	3.5	8.0	140.1	148.1	94.6
	90–120	Cca3	8.5	7.4	8.6	0.7	11.6	247.0	187.2	6.4	1.1	8.6	3.6	203.3	206.9	98.3
P2	0.5–22	Ah	7.8	6.7	44.9	3.7	12.2	80.0	144.4	7.6	1.3	3.8	13.4	157.1	170.5	92.1
	22–33	AB	8.2	6.6	25.7	2.4	10.5	11.0	200.4	4.4	1.2	6.1	8.0	212.2	220.2	96,3
	33–60	Bw	8.5	6.8	20.7	1.0	21.1	5.0	187.7	5.6	1.9	5.3	10.7	200.4	211.1	94.9
	60–85	BC	8.7	7.1	14.7	0.9	16.0	121.0	159.2	3.7	1.2	5.1	6.3	169.3	175.5	96.4
	85–110	2Cca1	8.7	7.1	12.6	0.8	16.5	173.0	193.5	5.8	3.9	5.3	6.3	208.5	214.8	97.1
	>110	2Cca2	8.5	6.8	10.8	0.7	14.4	182.0	225.0	8.5	2.1	6.6	5.4	242.1	247.5	97.8
P3	2–7	Ahca	7.3	6.5	89.0	4.9	18.1	28.0	157.8	6.0	1.5	5.2	8.0	170.5	178.5	95.3
	7–20	Aca	8.2	6.8	39.5	2.4	16.7	94.0	189.0	6.7	1.5	4.4	8.0	201.5	209.6	96.2
	20–33	Cca1	8.8	7.1	16.7	0.6	29.0	363.0	141.6	21.2	2.5	6.5	5.4	171.8	177.2	96.9
	33–50	Cca2	8.7	7.3	7.5	0.5	15.3	370.0	186.1	24.6	1.7	7.4	6.3	219.7	226.0	97.2
	50–90	Cca3	8.6	7.3	5.7	0.5	12.8	260.0	120.5	20.8	1.6	7.2	7.1	150.1	157.3	95.5
P4	0–2	Ah	6.2	5.7	79.4	5.6	14.2	0.0	204.5	27.0	3.0	16.0	7.5	250.5	258.0	97.1
	2–10	A	6.0	5.4	49.4	3.6	13.7	0.0	189.0	19.0	3.0	9.0	5.0	220.0	225.0	97.8
	10–35	AB	6.4	5.1	19.3	1.7	11.4	0.0	208.5	12.0	2.0	6.0	3.6	228.5	232.1	98.4
	35–60	BC	6.4	5.1	n.d.	n.d.	n.d.	0.0	207.5	10.0	3.0	5.0	3.2	225.5	228.7	98.6
	60–90	2Cca	8.0	7.0	n.d.	n.d.	n.d.	274.0	217.0	5.0	2.0	5.0	1.1	229.0	230.1	99.5

Explanation: TPA – total potential acidity; TEB – total exchangeable bases; ECEC – cation exchange capacity; BS – base saturation; n.d. – not determined.

DISCUSSION

According to PSC (2011) four types of carbonate-rich soil can be distinguished – rendzinas (raw rocking rendzinas, proper rendzinas, brown rendzinas and chernozemic rendzinas), pararendzinas, soils with the admixture of allochtonous silicate materials, named mixed rendzinas and typical eutrophic brown soils. Nowadays, distinction of those soils can occur only through their chemical and physical properties as well as varied parent material from which those soils may derived. Based on the division by PSC (2011) and field research, analysed soils supposed to be classified as pararendzinas. However, there are some shortcomings, which provide a basis for discussion about the detailed criteria as well as the place of pararendzinas in PSC (2011), especially according to the soils formed on the slopes of the mountain's areas.

Traditional approach assumed that the type of parent material of carbonate-rich soil from the Pieniny Mts. area has the decisive influence on shaping their physical and chemical properties (Zasoński 1992, Skiba et al. 2002, Kacprzak 2003, Kabała et al. 2008, Lasota et al. 2014). Nevertheless, analysed soils have been formed from weathering alterations of rock material dislocated on the slopes with stratified arrangement named cover beds (Kasprzak and Derkowski 2007). Cover beds, especially in Pieniny Mts., contain both carbonate and non-carbonate material and are often enriched with admixture of foreign material. Hence, diverse particle size distribution within every profile is caused by various shares of parent material such as limestone, sandstone and shale within cover beds (Table 2).

Content of silt fraction was generally higher in humus horizons in comparison with deeper ones (e.g. profile P3), which is thought to be related with accumulation of eolian materials with the additions of autochthonic materials in surface horizons of studied soils (Zasoński 1981, Kacprzak and Żyła 2006, Kabała et al. 2008). Similarly, the amount of quartz and plagioclase is higher in upper horizons, which can be also result of eolian input of those minerals in the investigated soils (Fig.). In addition, a large diversity of individual grain fraction content between horizons (e.g. profiles P1, P2, P4) was connected with slopewash and solifluction processes (Zasoński 1981, Kacprzak and Skiba 2000, Kacprzak 2003). Taking into consideration the mineral composition it should be mentioned that only qualitative phase identification were performed, so it is impossible to estimate the exact proportions of soil forming minerals, but rough estimations due to intensity of the highest XRD peaks determine that the proportions of quartz and calcite varied from soil to soil (Fig.). The Figure also shows that the amount of calcite decreases in a upper parts of soil profile.

All analysed soils fulfil the diagnostic criterion for pararendzinas concerning carbonates content, i.e. they have more than 15% $CaCO_3$ in the parent material (PSC 2011). Content of $CaCO_3$ was varied in studied soils (Table 3) and mainly depended on different amounts of calcite in the parent material and selective weathering (Zasoński 1992). Moreover, the

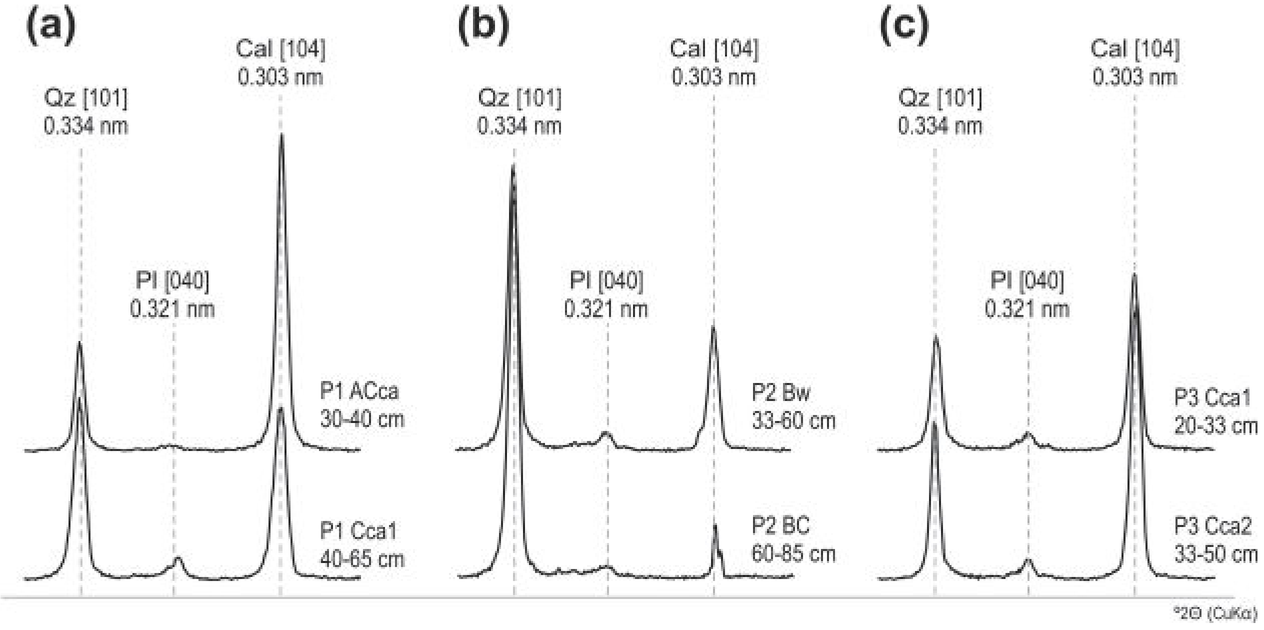

FIGURE. Fragments of X-ray diffraction patterns with peaks of quartz (101), plagioclase (040) and calcite (104) of raw powder samples from mineral horizons of soils P1 (a), P2 (b) and P3 (c).

investigated soils were characterized by the lower content or lack of $CaCO_3$ in the surface horizon or middle part of profiles (Table 3). Zasoński (1993) related the arrangement of $CaCO_3$ with the intensity of dissolution and leaching of carbonates in soil genetic horizon. According to his studies, pararendzinas formed from Carpathian's flysch were characterized by slow decalcitization, which includes both bedrocks fragments and weathered material, wherein the rate of decalcitization was slower in skeleton parts. In contrast to those studies, varied content of $CaCO_3$ within the analysed soils formed from cover beds, can be a result of impoverishment of carbonate rocks with calcium carbonate compunds during the transport. It can be stated that the lower content of $CaCO_3$ in the rock fragments can be also a result of additives of non-carbonate materials (Zagórski 2003, Kacprzak and Derkowski 2007).

Taking into consideration the admixture of foreign silicate material, it can be assumed that studied soil profiles could be classified as mixed rendzinas. Nevertheless, due to the fact that according to current PSC (2011) pararendzinas can be formed e.g. from sandstones, high content of quartz and silicate minerals is expected; thus the division based on the type of rock, is quite inconsistent in this case. Following the current division, given by PSC (2011), the admixture of silicate material could decide about belonging to individual groups (Kabała 2014).

Investigated soils were characterized by high content of organic carbon in surface horizons. In studied soils, organic carbon occurred even in the deepest horizons (Table 3). This is the result of translocation of organic matter and plant's deep-rooting within loose skeleton's soil material. A similar phenomenon was described by Zasoński and Skiba (1988), and Zasoński (1992, 1993). A large content of clay fraction in soils causes aggregates stabilization and carbon sequestration. According to Zasoński (1992), mineral colloids affect the stabilization of humic compounds in a B and C soil horizon. Likewise, on the aggregates stability, Ca^{2+} ions have a large influence (Ben-Hur et al. 1985, Amézkrta 1999).

Furthermore, sorption properties of carbonate-rich soils were mostly influenced by the impact of the carbonate bedrock and a large amount of carbonate rock fragments within the soil profile.Similar relationships were described by Zasoński (1993). A characteristic feature of carbonate-rich soils was high base saturation and especially large shares of Ca^{2+} cations (Zasoński 1992, 1993; Caravaca et al. 1999, Jonczak 2010, Tomašić et al. 2013). The large content of Ca^{2+} cations was related with abundance of $CaCO_3$ in parent material. According to Zasoński (1992) and Jaworska et al. (2008) it can be stated that some soils can cause minor extension of sorption capacity. The binding of calcium ions in soil is strong enough, hence the high concentration of Ca^{2+} ions occur despite the absence of or low content of $CaCO_3$ (e.g. profile P4) (Table 3).

The high sorption capacity and composition of sorption complex of studied soils were also influenced by large contents of organic carbon and high amount of clay fraction. The sorption is strongly related to the type of clay minerals. The 1.4 nm peak may indicate presence of the smectite, vermiculite or chlorite, but more analysis to provide more detailed identification of the clay fraction should be performed. The obtained results were similar to described for pararendzinas and rendzinas at the area of Tatra Mts. and Pieniny Mts. by several authors (Zasoński 1992, 1993; Jaworska and Długosz 1996, Zagórski 1999, Miechówka 2002).

Reaction within the studied soils, between the genetic horizons was variable and mostly depended on $CaCO_3$ content; thus, pH values increased with depth, where the content of $CaCO_3$ was higher (Table 3). Acidification of humus horizons caused the dissolution of $CaCO_3$ by organic acids which originated from the products of litter decomposition and forest vegetation (Miechówka 1989). This process has also resulted in higher total potential acidity in humus horizons than in the deeper horizons (Table 3).

Analysing the reaction within studied soils, initially classified as pararendzinas, can be stated that most horizons have higher pH values, measuring in H_2O than ranges (6.0–7.5) given by PSC (2011). Due to the fact that other properties (e.g. content of $CaCO_3$) made it possible to classify the studied soils as pararendzinas, perhaps upper limit of pH values given by PSC (2011) should be discussed. In particular, similar pH values in pararendzinas were described by other authors (Zasoński 1993, Kacprzak and Żyła 2006, Zaleski et al. 2006). The similar situation occurs in case of the soil`s depth criterion (the pararendzinas' thickness). Taking into consideration the guidelines given by PSC (2011) weakly developed soils should have not more than 50 centimetres depth. The thickness of all soil profile was more than 50 cm, thus, following this criterion, analysed soils should be automatically degraded from order of weakly developed soils. According to PSC (2011), there is no specific information about the pararendzinas, which caused the contradictions during the classification. It should be mentioned that in the previous edition of PSC (1989), pararendzinas could have thickness at least 50 cm. The authors suggest that the thickness of the weakly developed soil should be more clarified taking into account the specific conditions of these soils formation.

It should be mentioned, that according to PSC (2011), in the pararendzinas description (symbol sequence), presence of secondary (pedogenic) calcium carbonate within soil profile is necessary. However, the description of pararendzinas contains information that lithological (primary) calcium carbonate derived from the directly underlying weathered rocks (e.g. sandstones or shales) within the soil profile can be found as well. According to Kabała (2014) the following division has been proposed: rendzinas include the soils, where carbonates would be mainly primary, lithological origin (including lake chalk), whereas the soils, where carbonates originated mainly from pedological processes are considered as pararendzinas. Such approach could unambigously resolve the problem of rendzinas and pararendzinas separation.

Furthermore, in a situation where within the rendzinas', *cambic* horizon is forming, those soils should be classified as brown rendzinas. However, there is no such analogy for pararendzinas. Zasoński (1992) described pararendzinas with partially developed *cambic* horizon, that did not meet thickness criterion for brown soils' *cambic* horizon according to PSC (2011). It seems, that this type of soil should be considered as the transitional stage between pararendzinas and brown soils. Detailed analysis of P2 and P4 profiles allow to identity the *cambic* horizon within these soil profiles. According to PSC (2011) brown pararendzinas are characterized by occurrence of *cambic* horizon, but do not fulfil the thickness criterion. It should be mentioned that the *cambic* horizon within the P2 and P4 profiles have more than 15 cm (Table 2). In such as situation P2 and P4 profiles must be positioned in the order of brown earths soils, type typical eutrophic brown soils (PSC 2011). Nevertheless, based on the symbol sequence record of soil horizon given by PSC (2011), within the parent material of eutrophic brown soils the secondary calcium carbonate, similarly as in case of pararendzinas should be identified. Referring to Kabała (2014), following on this record, evolution of soil formed from parent material, which is rich in lithogenic calcium carbonate, would be impossible.

Detailed analysis of chemical and physical properties of profile P1, allowed for identification *mollic* horizon according to PSC (2011). Identification of *mollic* horizon within the soil profile is the foundation to classify profile P1 to the seventh order – black soils, type of chernozemic rendzinas. *Mollic* horizon within P1 is mainly the result of organic matter deposition from upper parts of the slope and in lesser degree as an effect of *in-situ* accumulation. However, classification of profile P1 as chernozemic rendzinas is limited by the criteria given by PSC (2011). P1 profile was characterized by high content of rock fragments in A horizon (Table 2) what did not meet the criterion for chernozemic rendzinas. Furthermore, according to rendzinas description, these soils were formed from carbonate or sulfate rocks and in PSC (2011) is no mention about even small amount of the non-carbonate rock fragments occurrence, which have been found in P1 profile classified as chernozemic rendzinas. Restrictions mentioned above concerning to carbonate and non-carbonate rock fragment are not included in IUSS Working Group WRB (2015). Nevertheless, there is no more suitable classification for this soil according to PSC (2011), what also reflect general problem with classification of carbonate-rich soils. Authors suggest that this aspect should be more clarified.

It can be assumed that studied soils could comply with most of criteria concerning pararendzinas given by PSC (2011) such as the type of parent material, $CaCO_3$ content, TOC content and saturation of sorption complex with bases. Nevertheless, P1 profile was classified as typical chernozemic rendzinas due to occurrence the *mollic* horizon. Moreover, within soils P2 and P4 *cambic* horizon have been formed, thus those soils were classified as brown earths soils. Some of soils' properties do not fulfil all of criteria for pararendzinas or those information are not given by PSC (2011). Among those criteria, the range of pH values, thickness of pararendzinas profiles, admixture of eolian silt as well as issue of secondary carbonate should be resolved. Based on the conducted research, the authors suggest that some of criteria concerning on carbonate-rich soil should be discussed and furthermore clarified, that includes in particular: i) determination of the boundary between rendzinas and pararendzinas; ii) clarification of the range of pH values and thickness for pararendzinas; iii) specification of the direction of pararendzinas evolution due to formation a *cambic* horizon iv) determination and field recognition of differences between primary and secondary carbonates.

CONCLUSIONS

1. Based on the research, some similarities of morphological, chemical and physical, as well as mineralogical features within the analysed carbonate-rich soils can be found. Nevertheless, despite the wide spectrum of carbonate-rich soils according to Polish Soil Classification (2011), there are some issues with unambiguous classification due to the occurrence of carbonate and non-carbonate

rock material within the soil profile. Authors noticed that carbonate-rich soil may be classified in to different units (orders, types).

2. The conducted studies have allowed to state that soils can be classified as: P1 – typical chernozemic rendzina, P2 and P4 – typical eutrophic brown soils, whereas P3 – typical pararendzina.
3. Taking into consideration determined chemical and physical properties, it can be found that investigated soils were influenced by not only the *in-situ* weathering material but also by rock material which have been transported and deposited as a result of slope processes. Furthermore, the lack or lower content of $CaCO_3$ in surface and middle part of analysed soils was most likely a result of the impoverishment of rock material during the transport on the slope.

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Zróżnicowanie morfologicznych, fizycznych i chemicznych właściwości gleb zasobnych w węglan wapnia na obszarze Pienin (południowa Polska)

Streszczenie: Gleby zasobne w węglan wapnia charakteryzują się dużym zróżnicowaniem udziału węglanowych lub niewęglanowych składników mineralnych w substracie glebowym, które decydują o ich właściwościach. W pracy przedstawiono wyniki badań czterech gleb pobranych z obszaru Pienińskiego Parku Narodowego. Celem badań była charakterystyka i klasyfikacja gleb wytworzonych z węglanowych i zasobnych w węglan wapnia materiałów macierzystych. Zostało to osiągnięte przez oznaczenie morfologicznych, fizycznych i chemicznych właściwości, jak również oznaczenie składu mineralogicznego wybranych gleb, bogatych w węglan wapnia, występujących w polskich Pieninach. Badane gleby zaklasyfikowano jako rędzinę czarnoziemną typową (P1), gleby brunatne eutroficzne typowe (P2, P4) oraz pararędzinę typową (P3) według kryteriów podanych przez Systematykę gleb Polski (2011)

Gleby położone były na stokach o różnym nachyleniu i ekspozycji. Materiałem macierzystym gleb P1, P2 i P4 były pokrywy stokowe z dominującym udziałem szkieletu pochodzącego z piaskowców oraz mniejszym udziałem szkieletu wapiennego. Gleba P3 wykształciła się z bogatych w kalcyt czerwonych łupków pstrych. Gleby charakteryzowały się trwałą strukturą agregatową: gruzełkową, angularną lub subangularną. Były średnio lub silnie szkieletowe, głównie o uziarnieniu glin z dużym udziałem frakcji pyłowej. Zawartość $CaCO_3$ zawierała się w granicach od 0,0 to 703,0 $g \cdot kg^{-1}$. Odczyn gleb był od lekko kwaśnego w poziomach próchnicznych do alkalicznego w poziomach spągowych. Gleby te cechowały się bardzo wysokim wysyceniem kompleksu sorpcyjnego przez kationy zasadowe, wśród których przeważały jony Ca^{2+}, co wynikało z węglanowego lub zasobnego w węglany materiału macierzystego i podłoża geologicznego. Wysoka pojemność sorpcyjna wynikała z dużej zawartości materii organicznej i frakcji iłowej. Biorąc pod uwagę chemiczne i fizyczne właściwości stwierdzono, że badane gleby wytworzone zostały nie tylko w wyniku wietrzenia skał *in-situ* ale były również wynikiem transportu i depozycji materiału skalnego podczas procesów stokowych. Niska zawartość lub brak $CaCO_3$ w górnej lub środkowej części profilu glebowego była związana z zubożeniem materiału skalnego w trakcie jego transportu po stoku.

Słowa kluczowe: gleby zasobne w węglan wapnia, gleby Karpat, Phaeozems, Cambisols, Regosols