ARCHIVES OF ENVIRONMENTAL PROTECTION

vol. 35 no. 2 pp. 97 - 104 2009

PL ISSN 0324-8461

HEAVY METALS AND SELECTED PHYSICOCHEMICAL PROPERTIES OF RENDZIC LEPTOSOLS OF THE PONIDZIE REGION (SOUTHERN POLAND)

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Keywords: Rendzic Leptosol, chemical properties, heavy metals, Nida Basin.

Abstract: The aim of the study was to characterize and compare physicochemical properties of Rendzic Leptosols formed in the Nida Basin. The highest heavy metal contents were observed in surface horizons. Average heavy metal contents were (mg·kg^{-1}): Zn – 59.9, Cu – 24.9, Pb – 23.4, Cr – 15.4. These values are typical of Rendzic Leptosols and moderate to heavy soils. The soils under study were characterized by high pH values, large content of organic matter, $CaCO_3$, high saturation of sorption complex with basic cations. The soils did not show greater differences in chemical properties.

INTRODUCTION

The vast, sloping south-westwards Nida Basin is a part of the Śląsko-Małopolska Upland and is characterized by an exceptional diversity of physicogeographical conditions. The formation of Limestone-Rendzic Leptosols was facilitated by transgression and regression of Cretaceous seas leading to the sedimentation of several hundred-meter deep series of limestones, chalk rocks and marls [10, 13]. Recurrent short-term return of a shallow sea to the area of the present Nida Basin in Tertiary period left a series of lithotamnic limestones, marls, glauconite sands and gypsum in the changing sedimentation condition zone [3, 8]. Gypsum accumulation and weathering processes promoted the formation of Sulfate-Rendzic Leptosols [4, 11]. The gypsum series occurring in the Ponidzie Region are characterized by a marked regularity and cover a large compact area. They are built mainly of three types of gypsum: selenite, compressed coarse-crystalline gypsum and shaley gypsum [13, 18].

The goal of the present study was to characterize and compare physicochemical properties of Cretaceous, Tertiary and Sulfate-Rendzic Leptosols formed in this area.

MATERIAL AND METHODS

This study investigated in detail 5 profiles of Rendzic Leptosols occurring in the Nida Basin. The profiles of Rendzic Leptosols (Fig. 1, Tab. 1) were sampled in 2004 in the following mesoregions: the Wodzisław Hummock (profile no. 1 near the town of Tomaszów), the Solec Basin (profile no. 2, near the town of Łatanice), the Pińczów Hummock (profile no. 3 near the town of Zakamień), the Połaniec Basin (profile no. 4 near the town of Kije and profile no. 5 near the town of Śladków Mały).

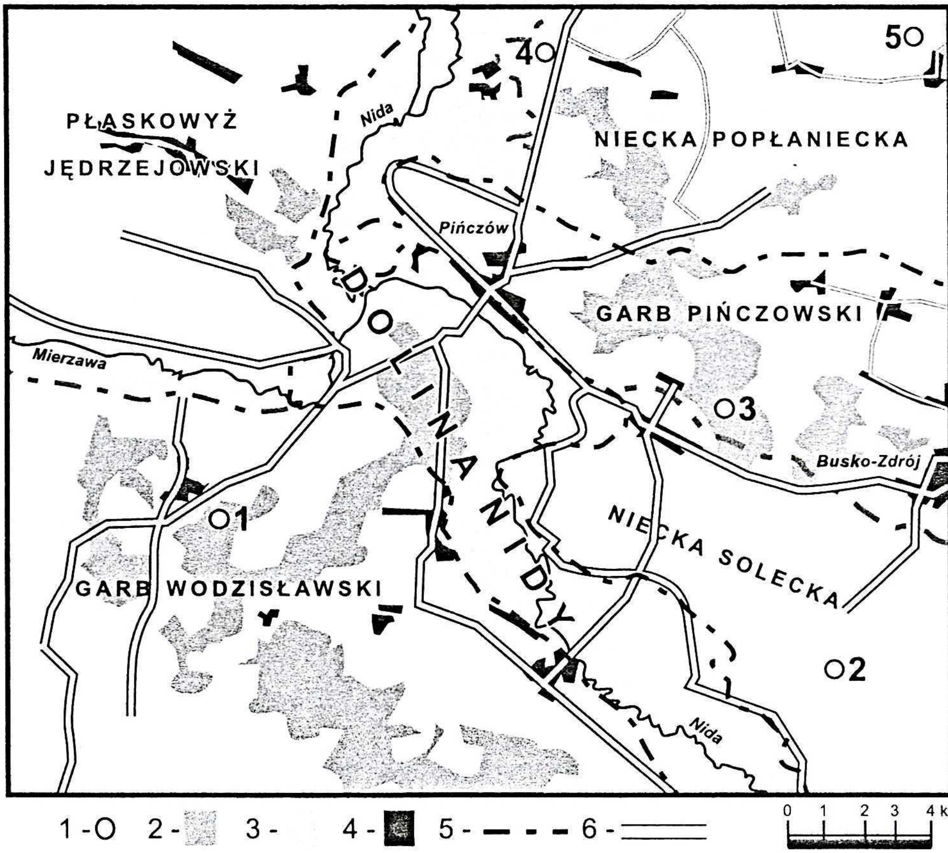

Fig. 1. Localization of soil profiles on the background of physicogeographical units
1 – no profile, 2 – forest area, 4 – grounds area 5 – physicogeographical units 6 – roat

Soil pits were dug to bedrock and 4–6 samples were collected from defined soil horizons for laboratory analyses. Air-dried samples were analyzed for particle-size distribution in the skeletal and gravel sands fraction by sieve analysis, and in the dust and floating fraction by aerometric method of Casagrande modified by Prószyński, pH in H_2O and in 1 M KCl was determined by a potentiometric method, $CaCO_3$ content by Sheibler calcimeter method, organic carbon content in mineral horizons by Tiurin method and in organic horizons by Alten method, total nitrogen content after sample mineralization by Kjeldhal method using a Kjeltec Auto 1030 autoanalyzer, hydrolytic acidity by Kappen method in 0.5 M $Ca(CH_3COO)_2$ solution, sum of basic exchangeable cations S was assayed in 0.5 M NH_4Cl, pH 8.2. Based on the sum of basic cations (S) and hydrolytic acidity (Hh), sorption capacity T and soil saturation with alkali V were calculated. Trophic index of forest soils ITGL was calculated based on weighed sum (I_{suma}) of the following

Table 1. Profile structure and general characteristic of soils

Profile No	Profile structure	Type and subtype	Kind	Species	Trophic index
Profile 1 Tomaszów	Ol-Ah-CcaA-Cca	Rendzic Leptosol	Cretaceous limestones	Normal dust on medium skeletal clay	ITGL 38.2 Hypertrophic
Profile 2 Łatanice	Ah-CcsA-Ccs	Gypsiri-Rendzic Leptosol	Gypsum	Medium clay on heavy skeletal clay	ITGL 40.5 Hypertrophic
Profile 3 Zakamień	Ol-Ah-ACcs-Ccs	Gypsiri-Rendzic Leptosol	Gypsum	Medium clay developed on dusty-skeletal formation	ITGL 40.2 Hypertrophic
Profile 4 Kije	Ah-CcaA-Cca	Rendzic Leptosol	Cretaceous limestones	Medium clay developed on clayey-skeletal formation	ITGL 36.1 Eutrophic
Profile 5 Śladków Mały	Ol-Ah-CcaA-Cca	Rendzic Leptosol	Tertiary limestones	Strong clayey sand on dusty-skeletal formation	ITGL 37.1 Eutrophic

indices: dust fraction (I_{dust}), floating fraction ($I_{c/s}$), pH (I_{pH}), basic exchangeable cations (I_{cat}) calculated per a volume unit, stage of organic matter decomposition ($I_{C:N}$) in relation to genetic mineral horizons of the soil under study, determined according to procedures proposed by Brożek [2]. Total contents of microelements and heavy metals in selected soil samples were determined by ICP-AES method using a Jobin-Yvon spectrometer, model JY 70 PLUS. Samples were dissolved in *aqua regia* solution: HCl-HNO_3, after prior incineration of organic substance at 480°C. 4 samples of the water collected in the vicinity of the profile 2 and 3 (Łatanice and Zakamień) were analyzed of the content for ions SO_4^{2-} and S^{2-} using photometer IF 205 SLANDI.

STUDY AREA

The Solec Basin is a spacious depression filled with Miocene sea deposits (mostly lithotamnic limestones and Thorton gypsums) formed on Cretaceous marls. The Solec Basin formations are complex and the basin is characterized by large fluctuations of relative altitude (to 50 m). Interesting gypsum series in the western part of the basin form a structural escarpment 35 m deep. Floor parts are formed by coarse-crystalline gypsums, middle part by coarse-crystalline transforming into cryptocrystalline gypsum with blade cleavage while approaching the surface [18]. Karst processes and phenomena developing in gypsums (sinks, ravines, and small caves) are an example of the most beautiful gypsum karst in Poland.

The Połaniec Basin is a flat-bottomed tectonic subsidence. The basin is filled by Miocene gypsums (interesting karst phenomena), silt and sands partially covered with Quaternary Sarmatian sediments encountered near the villages of Borkowo and Chrabkowo.

The Pińczów Hummock (Wójczańsko-Pińczowski) is a horst uplifted in Tertiary Period rising to an altitude of 293 m a.s.l. The hummock prominently dominates over the Nida Valley. It is covered by lithotamnic limestones ("Pińczów stone" – produced in Pinczów), marls and upper Cretaceous gaize, the same as in the adjacent basins, while the substratum contains marl and upper Cretaceous gaize. A middle part of the Pinczów Hummock is visibly lowered, and large areas are covered by glacial sands and moraine clays forming an accumulation plain.

The Wodzisław Hummock is a flat anticline of Cretaceous chalk rocks in the eastern part covered by loess. Loess covers the surface of the hummock but does not form a continuous cover. The loessial terrains are diverse owning to features of older substratum and Pleistocene and Holocene erosion processes.

RESULTS AND DISCUSSION

Soils occurring in the Nida Basin closely reflect litho logy of the parent rock, with prevailing lithogenic Limestone-Rendzic Leptosols, autogenic Cambisols, Chernozems, Haplic Podzols, and Fluvisols [11, 16].

The Rendzic Leptosols under study differed in the underlying parent rock and land use on its surface (arable land: profile 2 and 4, and land used for forest crops: profiles 1, 3, 5). They belonged to Cretaceous-Rendzic Leptosols (profile 1, 4), Tertiary-Rendzic Leptosols (profile 5) and Gypsiri-Rendzic Leptosols (profile 3 and 2), characteristic of this terrain [4, 6] (Tab. 1). Depth of these soils ranged from 35 to 68 cm. Mineral horizon Cca or Cce was usually strongly skeletal and contained weathered rock debris (12–76% of fraction > 1 mm), often transforming in the lower part into a massive rock (Tab. 2). Depth of humic horizon was much greater in Sulfate-Rendzic Leptosols and ranged between 30 and 50 cm. Granulometric composition of the fine fractions of soils under study comprised normal dust, medium clay, heavy clay and sporadically strong clayey sand (profile 5). They contained 20–68% of sand fraction, 13–44% of dust and 19–58% of floating particles.

The pH values of soils were in the range of 6.0–8.5. Horizons located directly above the parent rock had a slightly basic pH due to its influence (Tab. 3). The pH value decreased towards the surface, what can be attributed to the formation of organic acids able to chelate basic ions and to migrate towards the bottom of the profile. The pH value of organic horizon (pH in KCl) ranged from 6.2 to 7.4 and depended, among other things, on plant communities overgrowing the surface.

The soils contained different amounts of calcium carbonate which is another factor, apart from grain size distribution and parent rock, distinguishing the soils. Calcium carbonate content in surface horizons ranged between 1.6 to 13.8% and increased downwards in the profile to 67.2%.

The chemical analysis of waters collected in the nearness of profiles Gypsiri Rendzic Leptosols (the profile No. 2 and 3), a kind of fertile soil, showed the content of S^{2-} crossing 0.05 $mg \cdot dm^{-3}$. The content of ions SO_4^{2-} was very high and fluctuated from 390 $mg \cdot dm^{-3}$ (Łatanice) to 420 mg dm^{-3} (Zakamień), considerably exceeding the average content for natural waters which is situated within the range 10–80 mg dm^{-3} [7].

Waters about the high content of ions SO_4^{2-} are characterized by low pH values. However, pH analyzed samples of the water showed the insensible reaction with values in the section 7.40–7.92.

Table 2. Granulometric composition of investigated soils

Profile No	Horizons	Depth [cm]	% fraction with diameter [mm]						
			> 1.0	1.0–0.1	0.1–0.05	0.05–0.02	0.02–0.005	0.005–0.002	< 0.002
1	Ah	1–15	3.0	21.0	17.0	28.0	10.0	7.0	17.0
	CcaA	15–29	12.0	23.0	20.0	17.0	12.0	7.0	21.0
	Cca	29–55	38.0	25.0	21.0	13.0	13.0	8.0	20.0
2	Ah	0–31	2.0	41.0	4.0	3.0	10.0	9.0	33.0
	ACcs	31–49	5.0	32.0	6.0	5.0	7.0	12.0	38.0
	Ccs	49–52	12.0	31.0	8.0	7.0	9.0	13.0	32.0
3	Ah	2–49	3.0	32.0	5.0	15.0	10.0	12.0	26.0
	ACcs	49–60	22.0	20.0	10.0	14.0	46.0	5.0	5.0
	Ccs	60–68	76.0	38.0	8.0	36.0	9.0	5.0	4.0
4	Ah	0–20	25.0	39.0	6.0	13.0	14.0	15.0	13.0
	CcaA	20–30	31.0	30.0	15.0	12.0	9.0	10.0	24.0
	Cca	30–35	70.0	34.0	11.0	9.0	12.0	11.0	23
5	Ah	1–19	23.0	59.0	8.0	11.0	3.0	7.0	12.0
	CcaA	19–41	32.0	61.0	7.0	9.0	7.0	3.0	13.0
	Cca	41–50	57.0	68.0	5.0	8.0	4.0	9.0	6.0

It's the result of the dissolution reaction of the gypsum and the reduction of the solvable sulphate under of the organic matter:

$$CaSO_4{\cdot}2H_2O \rightarrow Ca^{2-} + SO_4^{2-} + 2H_2O \text{ and}$$
$$SO_4^{2-} + 2C_{org.} + 2H_2O \rightarrow H_2S + 2HCO_3^-.$$

These soils contained marked amounts of organic matter almost independently of the type of land use. The highest contents of organic carbon were observed in mollic horizon of Gypsiri-Rendzic Leptosols (3.96–5.32%), and the lowest in Ah horizon of Tretiary-Rendzic Leptosols (profile 5). The content of organic carbon in all profiles quickly decreased with depth.

The Rendzic Leptosols under study contained humus of calcimorphic type (kalcimull). C:N ratio in mineral horizons ranged from 3.3 to 13 and decreased with depth. Nitrogen content N_{TOT} was the highest in humic horizon of Rendzic Leptosols used for growing forest crops and fluctuated between 0.95–1.10. Hydrolytic acidity was low and amounted to from 6.5 cmol(+)·kg^{-1} in O horizon to 0.1 cmol(+)·kg^{-1} in Cca horizon. Sorption capacity was high, the sum of exchangeable cations was in the range of 23.9–104.8 cmol(+)·kg^{-1}. Sorption complex was saturated mainly by Ca^{2+}. These values are slightly higher than those reported by Ciarkowska [4, 5] for Gypsum Brown and Red-Rendzic Leptosols [15]. The highest values were characteristic of Gypsiri-Rendzic Leptosols in profile 3. Saturation of sorption complex of these soils was very high exceeding 87.1% (to 99.8%). Based on the features of soils expressed by trophic index ITGL, it can be inferred that these soils are hypertrophic and eutrophic (ITGL > 36.1, Tab. 1). Current richness of this habitat suggests a highland forest Lwyż-N with a potential vegetation represented by subcontinental dry-ground forest *Tilio-Carpinetum* (Tracz. 1962).

The highest contents of heavy metals in soils were observed in the surface horizons, which is in line with literature data [1, 5, 11, 15, 17]. Total contents of zinc in the study

Table 3. Some chemical properties of the investigated soils

Profile No	Horizons	Depth [cm]	pH H_2O	pH KCl	$CaCO_3$ [%]	C_{TOT}	N_{TOT}	C:N	Hh [cmol(+)·kg^{-1}]	S	T	V [%]	Zn [mg·kg^{-1}]	Cu	Pb	Cr
1	Ol	0–1	6.8	6.7	2.3	39.9	1.27	31.42	1.9	55.2	57.10	96.67	119.9	20.1	32.1	20.1
	Ah	1–15	7.1	6.9	13.1	3.77	0.29	13.00	1.1	56.1	57.20	98.08	90.2	15.8	26.2	18.9
	CcaA	15–29	7.6	7.2	33.2	0.71	0.08	8.88	0.6	42.5	43.10	98.61	37.4	10.9	5.1	11.9
	Cca	29–55	7.8	7.5	44.2				0.2	46.8	47.00	99.57	22.8	9.7	4.9	8.6
2	Ah	0–31	6.1	6.0	2.2	3.96	0.95	4.17	4.9	32.9	37.80	87.04	89.1	17.3	50.2	19.6
	ACcs	31–49	6.4	6.3	3.1	1.02	0.21	4.86	3.9	52.2	56.10	93.05	36.2	12.6	8.6	10.5
	Ccs	49–52	6.4	6.3	2.9				0.7	87.1	87.80	99.20	19.6	8.9	6.8	9.2
3	Ol	0–2	6.6	6.3	3.2	42.7	1.31	32.60	6.4	51.3	57.70	88.91	134.9	89.9	55.6	30.7
	Ah	2–49	7.0	6.5	7.1	5.32	1.01	5.27	4.3	41.9	46.20	90.69	109.5	80.9	49.1	25.8
	ACcs	49–60	7.5	7.2	11.8	1.12	0.32	3.50	0.6	104.8	105.40	99.43	88.9	60.4	26.4	20.1
	Ccs	60–68	7.7	7.3	5.2				0.2	123.6	123.80	99.84	30.2	20.1	10.3	7.2
4	Ah	0–20	7.1	7.0	13.8	4.20	1.19	3.53	1.1	43.9	45.00	97.56	49.4	15.9	20.1	10.1
	CcaA	20–30	7.3	7.1	25.8	0.76	0.09	8.44	0.5	47.9	48.40	98.97	28.8	11.8	4.9	6.8
	Cca	30–35	7.5	7.1	33.1				0.1	47.1	47.20	99.79	22.1	10.1	5.2	6.9
5	Ol	0–1	7.1	6.8	1.6	40.2	0.89	45.17	3.1	45.5	48.60	93.62	91.1	26.8	49.3	26.2
	Ah	1–19	7.8	6.9	12.9	1.55	0.23	6.74	1.8	41.3	43.10	95.82	71.2	21.7	45.2	21.4
	CcaA	19–41	8.2	7.2	41.8	0.88	0.08	11.00	0.5	35.9	36.40	98.63	67.1	17.5	21.8	14.8
	Cca	41–50	8.5	8.1	67.2				0.2	23.9	24.10	99.17	10.2	5.9	4.8	5.7

soils ranged from 10.2 to 134.8 mg·kg^{-1} (mean 59.9), of copper from 5.9 to 89.9 mg·kg^{-1} (mean 24.9), lead from 4.8 do 55.6 mg·kg^{-1} (mean 23.4), chromium from 5.7 to 30.7 mg·kg^{-1} (mean 15.4). These values are typical of Rendzic Leptosls and for heavy and medium-heavy soils [2, 4, 12, 17] Heavy metal contents in Rendzic Leptosols under study did not exceed permissible levels [9, 12]. Slight enrichment in copper (60–81 mg·kg^{-1}) was observed only in the mineral horizon of Gypsiri-Rendzic Leptosols, thus, this soil can be included into class I, i.e. soils with elevated Cu content for medium-heavy soils (where permissible content is 100 mg·kg^{-1}).

Information about the heavy metal content in the soils of Pińczów district [14] indicates that the concentration of these elements in the soils is relatively small. Values in soils to 10 cm are shaped as follows: Zn (14.8–178.8, mean 64.1 mg·kg^{-1}), Cu (1.8–23, mean 10.1 mg·kg^{-1}), Pb (5.1–93.3, mean 17.2 mg·kg^{-1}), Cr (0.13–1.5, mean 0.47 mg·kg^{-1}). The slight enrichment of superficial soil levels in heavy metals has an industrial character (The Pińczów Building Stone Works Joint Stock Company, Gypsum Industrial Plant "Dolina Nidy" S.A.) [11, 14].

CONCLUSIONS

1. The soils under study belong to the following subtypes: Cretaceous-Rendzic Leptosols, Tertiary-Rendzic Leptosols and Gypsiri-Rendzic Leptosols. They are skeletal soils of medium depth.
2. The soils are distinguished by high pH values, marked content of organic matter and $CaCO_3$, and high saturation of sorption complex with basic cations. They do not show much diversity in terms of the studied chemical properties.
3. Average contents of heavy metals in the Rendzic Leptosols were estimated (at mg·kg^{1}): Zn – 59.9, Cu – 24.9, Pb – 23.4, Cr – 15.4). These values are reported to characterize unpolluted soils.

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Received: August 25, 2008; accepted: February 2, 2009.

METALE CIĘŻKIE ORAZ WYBRANE WŁAŚCIWOŚCI FIZYCZNE I CHEMICZNE RĘDZIN PONIDZIA (POŁUDNIOWA POLSKA)

Celem prezentowanej pracy jest charakterystyka i porównanie właściwości chemicznych oraz zawartości metali ciężkich w rędzinach kredowych, trzeciorzędowych, siarczanowych wykształconych w obrębie Niecki Nidziańskiej. Najwyższe zawartości metali ciężkich stwierdzono w poziomach powierzchniowych. Przeciętna zawartość metali ciężkich wynosi (w $mg \cdot kg^{-1}$): Zn – 59,9; Cu – 24,9; Pb – 23,4; Cr 15,4) i są to wartości typowe dla rędzin i gleb średnio ciężkich i ciężkich. Badane gleby odznaczają się wysokimi wartościami pH, znaczną zawartością materii organicznej, $CaCO_3$, wysokim wysyceniem kompleksu sorpcyjnego kationami o charakterze zasadowym i nie wykazują większego zróżnicowania w obrębie badanych właściwości chemicznych.