

Characteristics of technogenic soils developed from Neogene and Quaternary sediments substrate on reclaimed sulphur and sand extraction mine sites

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Abstract

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This paper presents the diversity of Technosol properties at two post-mining sites: a reclaimed and afforested spoil heap of an opencast sulphur mine and a sandpit excavation, represented by Quaternary sands and loams, Neogene (Krakowiec) clays and mixtures of sands with clays. The investigated post-mining soils significantly differed not only in texture, but also in pH, sorption properties, and C and N content. The observed acidification and increase of C and N in the uppermost soil layers as compared to the parent material demonstrated how the organic matter that accumulates under the trees influences the soil-forming process. The acidification effect was not so clearly visible on clay soils due to their high buffer capacity. However, soils developed from Neogene clays were characterized by the highest organic carbon stock, which is associated not only with in situ accumulation, but also with geogenic carbon bitumens occurring originally in clays. Less carbon stock was observed in soils formed from mixtures of Quaternary sands and Neogene clays and from Quaternary loams and sands than in Neogene clays. The Technosols indicated progressive pedogenesis initiated by reclamation, which is mainly demonstrated by acidification and increase of C and N in the uppermost soil layers horizons compared to the parent rock.

1. Introduction

The large-scale transformations of the land surface and landscape associated with open-pit mining activities negatively impact the environment. As a result of this exploitation, post-mining facilities create above-ground external and internal dumps and deep excavations that radically change water relations both at the facility and in the ‘the cone of depression’ adjacent to open pit. Open-pit mining devastates the natural soil and plant cover and leaves exposed geological formations in the dumps to become parent rock for future soils (Bell and Donnelly, 2006).

After the occurrence of large-scale ecosystem transformations due to mining, the process of succession begins (Pietrzykowski and Krzaklewski, 2007; Woś et al., 2018). The long-term process of succession in post-mining sites is stimulated by anthropological intervention through reclamation and afforestation (Pietrzykowski and Krzaklewski, 2007). In post-mining sites, this process aims to restore the soil function of the newly exposed soil substrates (Rowland et al., 2009). For these reasons, mine-site rehabilitation is presented as an ideal case study for developing an ecosystem starting from point zero (Hüttl and Weber, 2001). Soils on ‘natural’ sites have evolved

over the centuries and their properties are affected and controlled by soil-forming factors like their parent rock, climate, water relations, relief, geographical location, plant cover and land use. Most of them are capable of self-regulation and are characterized by an efficient circulation of nutrients (Bednarek et al., 2011). Developing soils on post-mining sites are characterized by parent material intense transformations that are often derived from a mix of soil substrates from different geological strata, such as Quaternary, Neogene, and Carboniferous strata. These substrates are frequently unfavourable for vegetation and are characterized by properties very rarely found in natural soils: excessive acidification and alkalinity, deficiency of nutrients, low soil organic matter and unusual mineral composition (Pietrzykowski, 2014; Brevik and Lazari, 2014).

Due to the progress of science, the classification of soils formed from post-mining sites is constantly changing. According to Polish Soil Classification (Kabała et al., 2019), soils on post-mining sites belong to the anthropogenic soils order, and are called Industriosols. In accordance with the international classification IUSS Working Group WRB (2015), post-mining soils are classified as Spolic Technosols.

This study aimed to compare the properties (texture, pH, nutrient content, sorption complex properties, organic carbon

stock) of soils formed from Neogene clays and Quaternary sands in the reclaimed spoil heaps of an opencast sulphur mine and a sandpit excavation.

2. Study area

The study was carried out at two reclaimed and reforested sites in southern Poland: the spoil heap of a former open-pit sulphur mine Piaseczno (Tarnobrzeg region) and a sand pit mine excavation Szczakowa (Upper Silesia region), south Poland.

The spoil heap of Piaseczno mine is located in the Vistula Lowland (Solon et al., 2018; 50° 33.622' N, 21° 34.185' E; Fig. 1). In this region, the average annual air temperature is 8.9°C, and precipitation is 570 mm year⁻¹ in period 1990–2019 (source: <https://en.tutiempo.net>). The site is conical in shape with an area of 120 ha and a height of up to 40 m. The spoil heap mainly consists of Neogene clays of the Krakowiec formation, loose Quaternary sands and mixture of Quaternary sands and Neogene clays. During the first 2 years after reclamation carried out in 1970s, initial revegetation and soil stabilization occurred on the spoil heap. During this time, legumes (mainly sweet clover (*Melilotus albus* L.)) and grasses (e.g., ryegrass (*Lolium* spp.)) were sown, and mineral fertilization occurred twice with total doses of 80, 50 and 60 kg ha⁻¹ of NPK, respectively. In the most difficult areas, where vegetation death occurred due to adverse air-water properties of substrates, sweet clover and alfalfa (*Medicago sativa* L.) also were sown. Species mainly consisting of oak, pine, birch, larch and alder were planted on the flatter hilltops (Skawina, 1974; Ziemnicki, 1980; Węgorzek, 2003).

The Szczakowa sand mine pit is located in the Upper Silesia region, southern Poland (50° 14.394' N, 19° 25.140' E; Fig. 1). In this region, the mean annual air temperature is 8.8°C, and the precipitation averages 733 mm year⁻¹ in the period 1990–2019 (source: <https://en.tutiempo.net>). The open-strip mining resulted in about 3500 ha disturbed area with an excavated depth of 5–25 m. The deposits are genetically related to the fluvioglacial Quaternary sediments deposited in a pre-Quaternary morphological depression. The sedimentation of deposits filling the Biała Przemsza River valley occurred during the Middle Poland and Würm glaciations period and its approximate age can be defined to reach between 80 and 240 thousand years. In addition to quartz sands, loam layers were found in the deposit. Loam deposits were not removed but stored in the excavation area on the surface. In the studied section of the sand mine cast, reclamation began in the 1970s. Initial reclamation treatments included re-grading the surface and incorporating organic amendments (approximately 300 m³ ha⁻¹). The organic amendment was the preserved uppermost forest soil layer of the overlying pre-mining forest (average organic carbon content of 0.3–1.0%). Subsequent treatments consisted of a two-year fertilization cycle (140, 130 and 150 kg ha⁻¹ of NPK, respectively) and a two-year cycle of cultivating lupine (*Lupinus luteus*) and incorporating it into the soil as green manure. The sites were then reforested with Scots pine and a mixture of birch, larch, oak, black locust and alder (Pietrzykowski and Krzaklewski, 2009).

3. Materials and methods

A total of 20 plots were selected for the study, taking into account the lithological diversity of the post-mining study objects (Fig. 1). On the Piaseczno spoil heap, the plots were located on 40-year-old post-reclamation soils formed from Quaternary sands (QsP), Neogene clays (Nc) and mixed Quaternary sands and Neogene clays (QsNc). On the Szczakowa excavation, the plots were located on 30-year-old post-reclamation Quaternary sands (QsS) and Quaternary loamy sands and loams (Ql). All plots were established within pure stands of Scots pine (*Pinus sylvestris*) except for Nc plots, which were located in common oak (*Quercus robur*) stands.

On each plot, mixed soil samples were taken from the 0–5 cm (A horizon), 5–30 cm and 30–100 cm (C1 and C2 subhorizons). Samples with intact structures were independently collected with 250 cm³ cylinders to determine bulk density (BD). Samples of the organic (litter) horizons (O_{lf}) were collected within five 0.20 m² square sub-plots. Fresh litter-horizon samples were weighed to the nearest 1 g with an electronic balance, and mixed samples were considered representative of each plot.

The following properties were determined for mineral horizon: the texture was measured with a Fritsch GmbH Laser Particle Sizer ANALYSETTE 22; pH was measured potentiometrically in H₂O and 1 M KCl with a 1:2.5 soil-solution ratio; carbonate (CaCO₃) content was determined by Scheibler's volumetric method; the organic carbon (SOC) and total nitrogen (Nt) contents were determined using a LECO TruMac® CNS. Prior to carbon analysis, the soil samples were treated with 10% HCl to remove carbonates. The content of plant-available phosphorus (P₂O₅) was determined via the Egner–Riehm method, which used a calcium lactate extract ((CH₃CHOHCOO)₂Ca). The content of exchangeable cations (Ca²⁺, K⁺, Mg²⁺, Na⁺) were determined by extraction in 1 M NH₄Ac and analysis of extract using an ICP-OES iCAP™ 6000 Series spectrophotometer. Total acidity (Hh) was determined via Kappen's method. Cation exchange capacity (CEC) and base saturation (BS) were determined by the sum of exchangeable cations (TEB) and total acidity (Hh).

The organic (litter) horizon samples were oven-dried; the measured moisture loss was used to calculate dry mass. Dried samples were ground, the C and N content were determined using a LECO TruMac® CNS and pH was measured potentiometrically in 1 M KCl in a 1:5 ratio.

The carbon stocks (C_{stock}) in litter and mineral horizons were calculated using the following equations:

$$C_{\text{stock (litter)}} [\text{Mg ha}^{-1}] = M_{\text{olf}} [\text{Mg ha}^{-1}] \times \text{SOC} [\%] / 100 \quad (1)$$

$$C_{\text{stock (mineral)}} [\text{Mg ha}^{-1}] = \Sigma(\text{SOC} [\%] \times \text{BD} [\text{g cm}^{-3}] \times T [\text{cm}]) \quad (2)$$

where: M_{olf} is the dry mass of litter horizons; SOC is soil organic carbon content; BD is bulk density; T is the thickness of the soil horizons.

Statistical analyses were performed using STATISTICA 13.1 software (StatSoft, Inc.). The effects of substrate and depth on

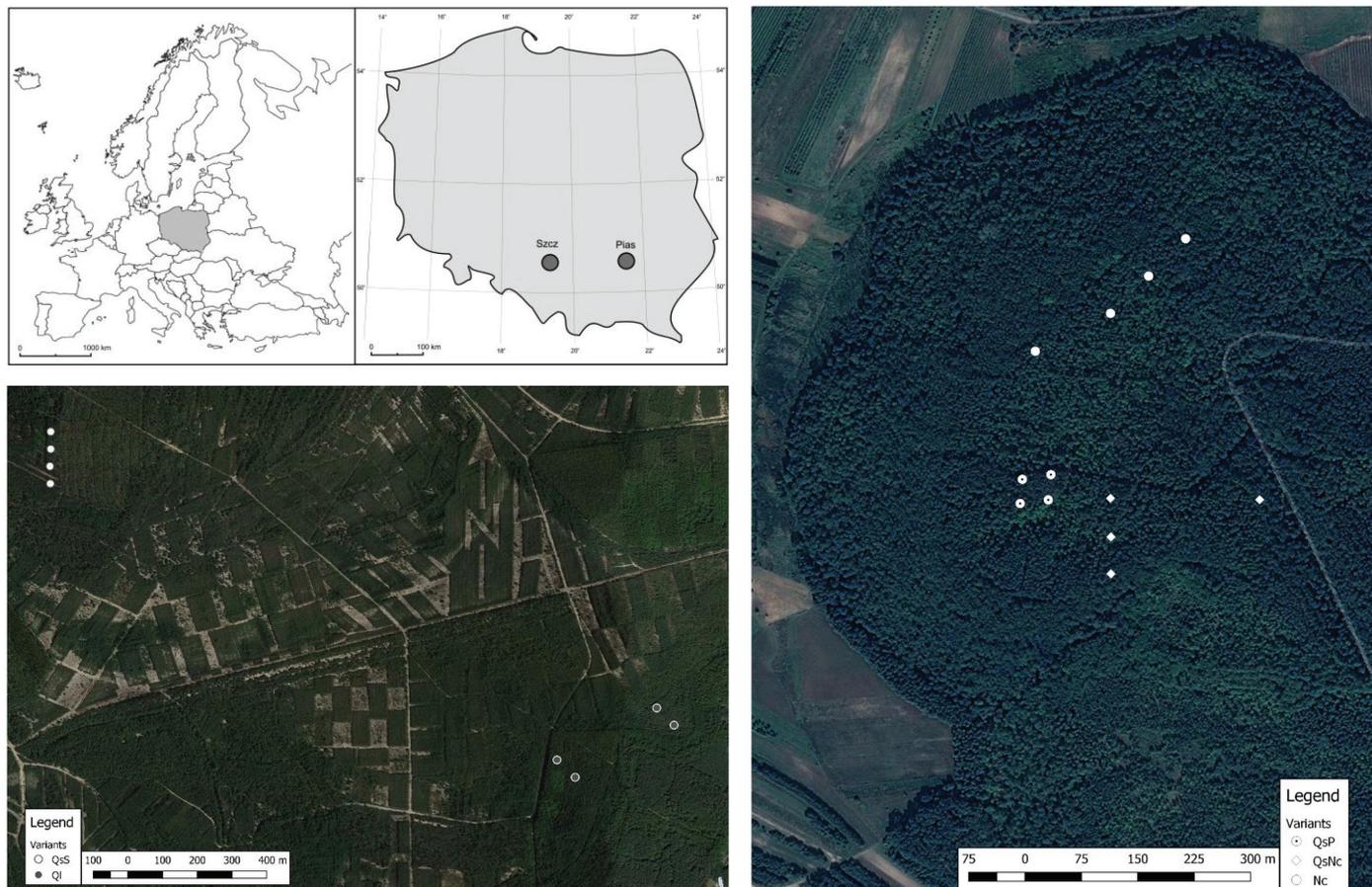


Fig. 1. Location of study sites: a) sand pit mine excavation Szczakowa, and b) spoil heap of sulphur mine Piaseczno

the studied technosol parameters were analysed using two-way ANOVA. The differences (significance assigned at $p < 0.05$) between mean values of the measured parameters were calculated using Tukey's test (HSD).

3. Results

Soils formed from Quaternary sands (QsP and QsS) were characterized by a sandy texture. Soils formed from mixed sands and clays (QsNc) were classified as loamy sands in the 0–5 and 30–100 cm horizons and sandy loams texture in the 5–30 cm horizon. Soils formed from Nc were characterized by a silty loamy texture. The texture of soils formed from Ql in different horizons varied. In 0–5 cm horizons, these soils were classified as loamy sands, in 5–30 cm sandy loams and in 30–100 cm silt loams. The BD in the tested soils had the lowest values in the 0–5 cm horizons (ranging from 1.02 g cm^{-3} on Nc to 1.34 g cm^{-3} on Ql). Carbonates (CaCO_3) were found in soils formed from Nc (from 139.5 to 165.1 g kg^{-1}) and QsNc (ranging from 0.8 to 1.6 g kg^{-1} ; Table 1).

Soil substrate and depth had significant effect on the pH value, SOC, Nt and P_2O_5 content (Table 2; Table 4). The soils formed on the sandpit had lower pH values compared to the soils formed on the open-cast sulphur mine spoil heap. The pH in H_2O

of sandpit mineral soil horizons ranged from 4.3 to 5.5, whereas the spoil heap's values ranged from 5.3 to 7.2. The lowest SOC content was found in soils developed from QsS (3.48 g kg^{-1}), and the highest in soils developed from Nc (38.80 g kg^{-1}). As in the case of SOC, soils formed from QsS displayed the lowest Nt content (0.08 g kg^{-1} in 0–5 cm horizon). The soils developed from Nc was characterized by the highest Nt content (3.03 g kg^{-1}). The P_2O_5 content was very low in soils formed from QsNc, QsS and Ql (ranging from 0.001 to 0.006 g kg^{-1}). The higher values were found in the 0–5 cm horizons of Nc (0.021 g kg^{-1}) and QsP (0.165 g kg^{-1}) soils (Table 2).

The soil substrate had significant effect on the sorption properties (exchangeable cations content, Hh, TEB, CEC and BS). The soil depth and interaction substrate \times soil depth had significant effect on Hh, K^+ and BS (Table 3; Table 4). The 0–5 cm horizons from QsP and Ql soils and all horizons from QsS were characterized by the prevalence of total acidity (Hh) ions in CEC. In other soils and horizons, Ca^{2+} cations dominated. The content of exchangeable cations in the investigated soils was as follows: $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+$. The soil formed from QsS displayed the lowest CEC values. The soils formed from Nc was characterized by the highest CEC values (Table 3).

The lowest C_{stock} values were found in soils developed from QsS (15.43 Mg ha^{-1}). The highest C_{stock} values were found in soils developed from Nc ($168.45 \text{ Mg ha}^{-1}$; Fig. 2).

Table 1
Texture, bulk density (BD) and CaCO₃ content in the investigated Technosols

Properties	Horizon [cm]	Variant					
		QsP	QsNc	Nc	QsS	Ql	
Sand (2.0–0.05 mm)	[%]	0–5	94 ±2 ^{c1}	75 ±3 ^b	6 ±1 ^a	91±3 ^{bc}	84±7 ^{bc}
		5–30	95 ±1 ^c	72 ±9 ^b	2 ±1 ^a	94±2 ^c	66±20 ^b
		30–100	96 ±0 ^d	75 ±7 ^c	2 ±1 ^a	95±1 ^d	42±16 ^b
Silt (0.05–0.002 mm)		0–5	5 ±1 ^a	23 ±2 ^b	78 ±2 ^c	8±3 ^a	15±6 ^b
		5–30	4 ±1 ^a	24 ±8 ^b	79 ±1 ^c	5±1 ^a	31±18 ^b
		30–100	3 ±0 ^a	22 ±6 ^b	77 ±1 ^d	4±1 ^a	52±14 ^c
Clay (< 0.002 mm)		0–5	1 ±0 ^a	3 ±0 ^a	16 ±2 ^b	1±0 ^a	2±1 ^a
		5–30	1 ±0 ^a	4 ±2 ^b	19 ±1 ^c	1±0 ^a	4±2 ^b
		30–100	1 ±0 ^a	3 ±1 ^b	21 ±1 ^d	1±0 ^a	6±2 ^c
BD	[g cm ³]	0–5	1.41 ±0.08 ^b	1.34 ±0.05 ^b	1.02 ±0.09 ^a	1.38±0.06 ^b	1.43±0.07 ^b
		5–30	1.58 ±0.07 ^b	1.49 ±0.06 ^b	1.24 ±0.10 ^a	1.52±0.03 ^b	1.67±0.08 ^b
		30–100	1.62 ±0.05 ^b	1.61 ±0.04 ^b	1.23 ±0.03 ^a	1.61±0.06 ^b	1.63±0.09 ^b
CaCO ₃	[g kg ⁻¹]	0–5	n.f. ²	0.8 ±0.7 ^a	165.1 ±17.2 ^b	n.f.	n.f.
		5–30	n.f.	1.6 ±2.4 ^a	163.0 ±25.8 ^b	n.f.	n.f.
		30–100	n.f.	1.3 ±1.4 ^a	139.5 ±68.8 ^b	n.f.	n.f.

¹ mean ± SD, different letters (a, b, c) indicate significant (p < 0.05) differences between the studied variants

² n.f. – not found.

Table 2
Reaction, carbon, nitrogen and available phosphorus content in the investigated soils

Properties	Horizon [cm]	Variant					
		QsP	QsNc	Nc	QsS	Ql	
pH in H ₂ O	Olf	4.4 ±0.2 ^{bc1}	4.8 ±0.3 ^c	5.9 ±0.2 ^d	3.9 ±0.1 ^a	4.1 ±0.2 ^{ab}	
	0–5	5.3 ±0.1 ^{ab}	5.7 ±0.7 ^b	7.1 ±0.1 ^c	4.7 ±0.1 ^a	4.3 ±0.1 ^a	
	5–30	6.3 ±0.9 ^b	6.4 ±0.6 ^b	7.0 ±0.2 ^b	5.1 ±0.1 ^a	4.9 ±0.4 ^a	
	30–100	7.0 ±0.6 ^b	6.6 ±0.9 ^b	7.2 ±0.2 ^b	5.5 ±0.1 ^a	5.3 ±0.4 ^a	
pH in KCl	Olf	3.7 ±0.2 ^{bc}	4.2 ±0.3 ^c	5.6 ±0.4 ^d	3.2 ±0.1 ^a	3.6 ±0.2 ^{ab}	
	0–5	4.4 ±0.1 ^a	5.0 ±0.9 ^b	6.7 ±0.0 ^c	3.9 ±0.2 ^a	3.7 ±0.2 ^a	
	5–30	5.7 ±0.8 ^b	5.6 ±0.9 ^b	6.6 ±0.2 ^b	4.1 ±0.1 ^a	3.9 ±0.4 ^a	
	30–100	6.4 ±0.6 ^b	5.8 ±1.2 ^b	6.8 ±0.1 ^b	4.4 ±0.1 ^a	4.2 ±0.4 ^a	
SOC	[g kg ⁻¹]	Olf	421.95 ±29.21 ^a	380.65 ±35.25 ^a	403.95 ±28.75 ^a	421.29 ±19.82 ^a	417.33 ±12.60 ^a
		0–5	7.56 ±4.21 ^a	18.39 ±3.56 ^b	38.80 ±4.70 ^c	3.48 ±0.79 ^a	7.58 ±2.52 ^a
		5–30	0.99 ±0.32 ^a	3.10 ±0.98 ^b	12.59 ±5.02 ^c	0.81 ±0.19 ^a	1.53 ±0.17 ^a
		30–100	0.40 ±0.11 ^a	1.41 ±1.26 ^b	12.20 ±1.78 ^c	0.13 ±0.03 ^a	0.40 ±0.11 ^a
Nt		Olf	11.63 ±0.91 ^a	11.62 ±1.52 ^a	18.33 ±1.41 ^a	10.12 ±0.84 ^a	11.25 ±1.38 ^a
		0–5	0.29 ±0.18 ^a	1.02 ±0.20 ^b	3.03 ±0.49 ^c	0.08 ±0.02 ^a	0.24 ±0.08 ^a
		5–30	0.01 ±0.01 ^a	0.17 ±0.05 ^b	0.84 ±0.31 ^c	0.01 ±0.00 ^a	0.03 ±0.03 ^a
		30–100	n.f. ²	0.09 ±0.10 ^a	0.55 ±0.11 ^b	n.f.	0.02 ±0.01 ^a
P ₂ O ₅		0–5	0.165 ±0.109 ^b	0.006 ±0.003 ^a	0.021 ±0.003 ^a	0.001 ±0.001 ^a	0.002 ±0.002 ^a
		5–30	0.007 ±0.014 ^a	0.006 ±0.004 ^a	0.012 ±0.001 ^a	0.001 ±0.000 ^a	0.001 ±0.000 ^a
		30–100	n.f.	0.004 ±0.004 ^a	0.011 ±0.003 ^a	0.001 ±0.000 ^a	0.001 ±0.000 ^a

¹ mean ± SD, different letters (a, b, c) indicate significant (p < 0.05) differences between studied variants.

² n.f. – not found.

Table 3
Sorpton complex properties in the investigated post-mining soils

Properties	Horizon [cm]	Variant				
		QsP	QsNc	Nc	QsS	QI
Hh [cmol(+) kg ⁻¹]	0-5	2.06 ±0.18 ^{a1}	3.70 ±1.23 ^b	1.21 ±0.06 ^a	1.96 ±0.23 ^a	3.53 ±0.71 ^b
	5-30	0.67 ±0.14 ^a	1.12 ±0.23 ^a	0.90 ±0.06 ^a	0.96 ±0.13 ^a	1.55 ±0.38 ^a
	30-100	0.55 ±0.17 ^a	0.86 ±0.25 ^a	0.80 ±0.08 ^a	0.70 ±0.03 ^a	1.35 ±0.33 ^a
Ca ²⁺	0-5	1.34 ±0.56 ^a	5.71 ±1.59 ^a	42.31 ±2.95 ^b	0.39 ±0.19 ^a	0.63 ±0.39 ^a
	5-30	0.90 ±0.42 ^a	5.30 ±4.15 ^a	48.58 ±9.08 ^b	0.42 ±0.08 ^a	1.66 ±0.82 ^a
	30-100	1.89 ±2.44 ^a	5.65 ±4.02 ^a	60.99 ±19.89 ^b	0.40 ±0.02 ^a	3.72 ±0.94 ^a
K ⁺	0-5	0.05 ±0.01 ^a	0.13 ±0.04 ^a	0.92 ±0.10 ^b	0.05 ±0.01 ^a	0.07 ±0.02 ^a
	5-30	0.03 ±0.01 ^a	0.05 ±0.02 ^a	0.61 ±0.10 ^b	0.03 ±0.01 ^a	0.10 ±0.03 ^a
	30-100	0.02 ±0.01 ^a	0.05 ±0.03 ^a	0.68 ±0.30 ^b	0.03 ±0.01 ^a	0.14 ±0.03 ^a
Mg ²⁺	0-5	0.13 ±0.06 ^a	0.54 ±0.01 ^b	1.18 ±0.21 ^c	0.11 ±0.05 ^a	0.14 ±0.09 ^a
	5-30	0.01 ±0.01 ^a	0.29 ±0.13 ^{ab}	0.68 ±0.52 ^c	0.15 ±0.04 ^a	0.53 ±0.25 ^{bc}
	30-100	0.01 ±0.00 ^a	0.35 ±0.24 ^{ab}	1.17 ±0.78 ^c	0.18 ±0.03 ^a	0.87 ±0.20 ^{bc}
Na ⁺	0-5	0.01 ±0.01 ^a	0.02 ±0.00 ^a	0.07 ±0.01 ^b	0.01 ±0.00 ^a	0.02 ±0.00 ^a
	5-30	0.01 ±0.01 ^a	0.02 ±0.01 ^a	0.07 ±0.01 ^b	0.01 ±0.00 ^a	0.02 ±0.01 ^a
	30-100	0.01 ±0.01 ^a	0.02 ±0.01 ^a	0.06 ±0.00 ^a	0.01 ±0.00 ^a	0.02 ±0.00 ^a
TEB	0-5	1.53 ±0.63 ^a	6.40 ±1.61 ^a	44.49 ±3.11 ^b	0.56 ±0.25 ^a	0.87 ±0.50 ^a
	5-30	0.96 ±0.42 ^a	5.66 ±4.25 ^a	49.93 ±9.49 ^b	0.62 ±0.12 ^a	2.31 ±1.10 ^a
	30-100	1.92 ±2.44 ^a	6.07 ±4.23 ^a	62.91 ±20.77 ^b	0.61 ±0.05 ^a	4.76 ±1.16 ^a
CEC	0-5	3.59 ±1.10 ^a	10.11 ±0.75 ^b	45.70 ±3.16 ^c	2.53 ±0.42 ^a	4.39 ±1.13 ^a
	5-30	1.63 ±0.28 ^a	6.78 ±4.01 ^a	50.83 ±9.46 ^b	1.58 ±0.21 ^a	3.86 ±1.43 ^a
	30-100	2.47 ±2.44 ^a	6.93 ±4.11 ^a	63.71 ±20.81 ^b	1.32 ±0.05 ^a	6.12 ±1.04 ^a
BS [%]	0-5	41.74 ±6.82 ^a	63.03 ±12.84 ^b	97.36 ±0.08 ^c	21.6 ±7.44 ^a	18.66 ±7.02 ^a
	5-30	56.80 ±16.35 ^a	78.91 ±10.45 ^b	98.16 ±0.46 ^c	39.1 ±4.04 ^a	57.81 ±9.67 ^a
	30-100	63.84 ±24.69 ^{ab}	82.35 ±14.76 ^b	98.61 ±0.56 ^c	46.5 ±2.66 ^a	77.32 ±7.28 ^b

¹ mean ± SD, different letters (a, b, c) indicate significant differences between the variants.

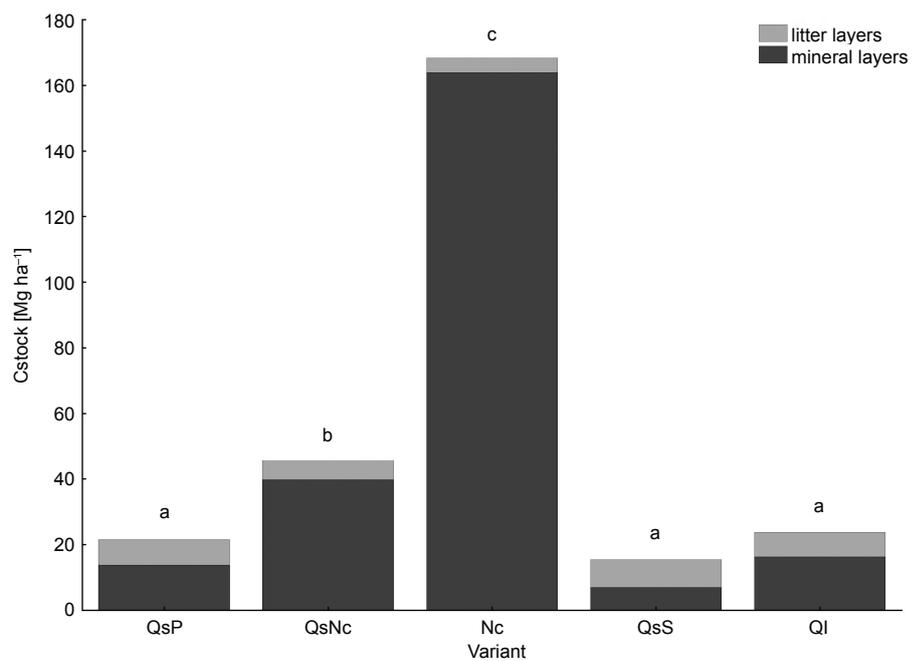


Fig. 2. Carbon stocks (C_{stock}) in investigated post-mining soils. Means followed by different letters (a, b, c) are significantly different

Table 4
Two-way ANOVA results for properties of Technosols on investigated post-mining sites

Properties	Substrate		Soil depth		Interaction Substrate × Soil depth	
	F	p	F	p	F	p
Sand	289.00	0.0000	5.76	0.0059	6.68	0.0000
Silt	233.33	0.0000	4.08	0.0235	6.83	0.0000
Clay	551.71	0.0000	16.08	0.0000	5.09	0.0002
CaCO ₃	152.11	0.0000	n.s. ¹	n.s.	n.s.	n.s.
pH in H ₂ O	49.89	0.0000	20.50	0.0000	n.s.	n.s.
pH in KCl	51.57	0.0000	10.43	0.0002	n.s.	n.s.
SOC	130.58	0.0000	154.60	0.0000	19.95	0.0000
Nt	150.45	0.0000	132.22	0.0000	40.26	0.0000
P ₂ O ₅	7.72	0.0001	9.42	0.0004	7.70	0.0000
Hh	17.49	0.0000	85.58	0.0000	5.78	0.0001
Ca ²⁺	159.40	0.0000	n.s.	n.s.	n.s.	n.s.
K ⁺	145.83	0.0000	4.74	0.0136	2.93	0.0102
Mg ²⁺	23.06	0.0000	n.s.	n.s.	n.s.	n.s.
Na ⁺	192.52	0.0000	n.s.	n.s.	n.s.	n.s.
TEB	155.30	0.0000	n.s.	n.s.	n.s.	n.s.
CEC	152.11	0.0000	n.s.	n.s.	n.s.	n.s.
BS	61.93	0.0000	29.80	0.0000	4.00	0.0012

¹ n.s. – not significant (p < 0.05).

4. Discussion

One of the most important stages of soil-forming process in post-mining sites is the accumulation of organic matter in the uppermost soil horizons (Pietrzykowski and Krzaklewski, 2007; Brevik and Lazari, 2014.). In the investigated soils, the SOC increase in the 0–5 cm horizons (ranging from 3.35 g kg⁻¹ in PczS to 26.60 g kg⁻¹ in Nc) as compared to the parent rock (30–100 cm). The C_{stock} in QsP, QsNc, QsS and Ql had lower values, and in the case of Nc higher values, than previously reported for forest soils in ‘natural’ sites. Data from the National Forest Soil Inventory (NFSI) indicate that the C_{stock} in soil horizons (up to 100 cm deep) at locations throughout Poland is, on average, 26 Mg ha⁻¹ in the organic horizons and 66 Mg ha⁻¹ in the mineral horizons (Gruba and Socha, 2019). These values were similar in the organic horizons and lower in the mineral horizons (up to 1 meter deep) than reported in applicable European forests literature (22.1 Mg C ha⁻¹ and 108 Mg C ha⁻¹, respectively) (De Vos et al., 2015), which the authors explain is due to the propensity of pine stands to grow on poor sandy soils in Poland (Gruba and Socha, 2019). However, the study’s results are consistent with the ranges observed in other post-mining sites. Vindušková and Frouz (2013) reported that the C_{stock} in post-mining soils in the northern hemisphere (Europe and the USA) can range from 4.49 to 93.20 Mg ha⁻¹. Pietrzykowski and Daniels (2014) found that the C_{stock} (up to 110 cm) in soils at various post-mining sites in Poland ranges from 16.8 Mg ha⁻¹ in the Quaternary sands of the Szczakowa mine to 2975.2 Mg ha⁻¹ in the carbonaceous shales of the Smolnica overburden spoil heap. However, such an extremely high C_{stock} resulted from the presence of hard coal on the Smolnica heap.

The higher values noted in soils developed from QsNc and Nc confirmed the fact that soils with a higher silt and clay content are typically characterized by a higher content of organic carbon. This difference is due to SOC binding by clay particles in the form of organic-mineral complexes. These complexes are resistant to leaching and microbiological degradation (Laird et al., 2001; Jimenez and Lal, 2006). The highest C content, observed in QsNc and Nc soils, was also due to the fossil (geogenic) carbon that accumulated in previous geological epochs during clay deposition (Pawłowski et al., 1985). The fossil carbon affects the overall soil carbon balance in initial ecosystems; it is also important for soil water retention (Fettweis et al., 2005; Frouz, 2016). However, the process of its incorporation into the biogeochemical cycle has not been thoroughly studied, although it is known that soil microorganisms play a key role in the process (Rumpel and Kögel-Knabner, 2003; Fettweis et al., 2005; Frouz, 2016). Determining the amount of fossil carbon in the total organic carbon pool in post-mining soils is difficult from a methodological point of view (Chabbi et al., 2008). The content of fossil carbon was determined based on the degree of ¹⁴C radioactive isotope decay (Rumpel and Kögel-Knabner, 2003) and via formulas that take into account specific post-mining site indicators (Amichev et al., 2008). Due to the young age of the studied soils and relatively poor accumulation of organic matter from decomposition in situ, the content of geogenic carbon can be approximated by the C content in the parent rock horizons (Vindušková and Frouz, 2013). This value averaged 1.41 g kg⁻¹ for QsNc and 12.20 g kg⁻¹ for Nc clays. Gruszczyński et al. (2012) reported slightly lower values in the nearby Machów mine, indicating that the Neogene (Krakowiec) clays have an organic carbon content ranging from 6.0 to 10.0 g kg⁻¹.

Dynamic of pedogenesis is also indicated by an increase in the Nt content (ranging from 0.08 g kg⁻¹ on QsS to 2.48 g kg⁻¹ on Nc) in 0–5 cm horizons as compared to the parent rock. As in the case of SOC, the higher Nt content in soils formed from QsNc and Nc is partly due to the genesis of the Neogene clays, and not as a result of accumulation in situ (Pietrzykowski et al., 2010). The content of fossil N accumulated in clays can be approximated in the parent rock horizons at 0.09 g kg⁻¹ in QsNc and 0.55 g kg⁻¹ in Nc. There is conflicting information regarding the fossil N availability for soil microorganisms and its incorporation into the biological cycle. Studies carried out at the hard coal mining spoil heaps indicate that the N contained therein is a heterocyclic compound and is therefore unavailable to plants and not included in biological circulation (Strzyszc and Hara-bin, 2004). Research performed at the post-mining sites after lignite exploitation indicates that N availability from lignite was low in young stands and higher in older stands (Hüttl and Weber, 2001).

One of the most frequently observed processes in the early stages of the pedogenesis on reclaimed post-mining sites is a decrease in the pH value in uppermost soil horizons (Pietrzykowski and Krzaklewski, 2009). The decrease in pH measured in H₂O from the 0–5 cm horizons as compared to parent rock ranged from 0.12 in Nc to 1.75 in QsP, whereas the difference in KCl ranged from 0.07 in Nc to 2.07 in QsP. The lack of a significant decrease in the pH of soils formed from Neogene clays was due to this substrate's high buffer capacity and carbonates content (Józefowska et al., 2019).

The quantitative series of exchangeable cations in the studied soils (Ca²⁺ > Mg²⁺ > K⁺ > Na⁺) was similar to natural soils occurring in the temperate climate zone (Bednarek et al., 2011). As with the decrease in pH value, the increase in total acidity (Hh) in uppermost soil horizons as compared to the parent rock levels is an indicator of pedogenesis.

The available phosphorus content in the studied soils was low, indicating a deficit of this element (Baule and Fricker, 1973). Phosphorus deficiency in soils has been reported in other post-mining sites reclaimed for forestry (Pietrzykowski et al., 2010).

5. Conclusions

The obtained results permitted drawing the following conclusions:

- The investigated technogenic soils significantly differed not only in texture, but also in pH, sorption properties, C and N content.
- The soils formed from Neogene clays were characterized by the highest carbon stock, which is associated not only with in situ accumulation of soil organic matter, but also with geogenic carbon bitumens occurring originally in clays.
- The technogenic soils properties indicated progressive pedogenesis which is demonstrated by acidification and increase of C and N content in the uppermost soil horizons compared to the parent rock.

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Właściwości gleb technogenicznych kształtujących się z substratów neogeńskich i czwartorzędowych na zrehabilitowanych terenach po odkrywkowej eksploatacji siarki i piasków podsadzkowych

Słowa kluczowe

Technosole
Industriosole
Rekultywacja
Zapas węgla
pH gleby

Streszczenie

W pracy przedstawiono zróżnicowanie właściwości gleb technogenicznych na dwóch obiektach pogórnich: zrehabilitowanych i zalesionych zwałowisku po odkrywkowej kopalni siarki i wyrobisku piasków podsadzkowych zbudowanych odpowiednio z glin i piasków czwartorzędowych, ilów Neogeńskich (Krakowieckich) oraz mieszanin czwartorzędowych piasków z ilami Neogeńskimi. Badane gleby pogórnice istotnie różniły się nie tylko uziarnieniem, ale także pH, właściwościami kompleksu sorpcyjnego oraz zawartością węgla i azotu. Obserwowane zakwaszenie i wzrost zawartości węgla i azotu w wierzchnich poziomach glebowych w porównaniu do poziomów skały macierzystej wskazywały na zaznaczające się coraz silniej oddziaływanie gromadzonej pod drzewostanami materii organicznej. Efekt zakwaszenia nie ujawnił się tak wyraźnie jedynie na glebach tworzących się na ilach, ze względu na ich znaczne zdolności buforowe. Jednakże, gleby wykształcające się z ilów Neogeńskich charakteryzowały się jednak największym zapasem węgla organicznego, związanego nie tylko z akumulacją *in situ*, ale także z zawartością geogenicznego węgla w bituminach ilów. Mniejszym zapasem węgla charakteryzowały się powstające gleby pogórnice w kolejności na mieszaninach czwartorzędowych piasków z neogeńskimi ilami, z glin i piasków czwartorzędowych. Stwierdzone wartości większego zakwaszenia oraz większej zawartości C i N w wierzchnich poziomach glebowych w porównaniu do poziomów skały macierzystej świadczą o postępującym procesie glebotwórczym w badanych glebach pogórnich, zainicjowanym w wyniku przeprowadzonej rekultywacji leśnej.