Lignite is still one of the main energy sources in many countries. Its opencast exploitation causes a lot of changes in the environment. After mining activities are created new and enduring relief forms such as internal and external dumping ground. The dumps consist of rocks conglomerate lying above the exploited mineral. As a result of reclamation, soil develops of this specific material. The aim of this study was to assess chemical properties of soils developing in post-mining areas of the lignite basin in the Wielkopolska region. The study included analyses of the effect of alfalfa (Medicago sativa L.) grown with orchard grass (Dactylis glomerata L.) on chemical properties of soils in 3 mineral fertilisation variants (0NPK – control, 1NPK and 2NPK). The experiments showed that the analysed soils retained the alkaline reaction, calcium carbonate and available magnesium contents as well as CEC from the parent material. The analyses confirmed a significant effect of both Medicago sativa L. and mineral fertilisation on chemical properties of tested soils. Cultivation of Medicago sativa L. in the 0NPK variant caused a statistically significant increase in SOC, TN and CEC in the Ap topsoil horizons. Mineral fertilisation additionally enhanced the accumulation of SOC, TN, P2O5 and K2O as well as an increase in CEC value. It needs to be stressed that irrespective of the adopted fertilisation level the investigated soils were characterised by higher SOC, TN, CEC and available Mg contents compared to means values of these parameters reported in arable mineral soils in Poland.

1. Introduction

Carbon is the primary energy source in many countries worldwide. In Poland almost 80% electric energy is generated from coal, of which approx. 1/3 is obtained using lignite (Widera et al., 2016; EurocoaL, 2018). The latter raw material is excavated by strip mining, which is the cheapest and simplest technology. However, it leads to several adverse changes in the natural environment. These changes are related with drastic disturbances in the hydrological regime in the area adjacent to the strip mine, elimination of vegetation as well as changes of the relief and landscape of the mining area (Kumar et al., 2015). During the mine’s work related to the removal of the rock overburden, transport and deposition of rock material in spoil banks, the original geological structure and soil are completely destroyed (Zhang et al., 2014; Ahirwal and Maiti, 2018). They are replaced with new land, which is typically characterised by nutrient deficits, adverse physical properties (Pająk and Krzaklewski 2007), disturbed water retention capacity as well as reduced microbial population and their activity (Placek–Lapaj et al., 2019). A characteristic feature of post-mining areas, as reported by Liu and Lal (2013), is related to the presence of rocks of varied geological origin, mineral composition as well as physical and chemical properties. Otremba and Gilewska (2013) stated that in the Konin-Turek Lignite Basin the post-mining areas are a conglomerate of Quaternary boulder loam of the Vistulian and the Warthian glaciation, Quaternary sands, Neogene Poznan clays and sporadically Neogene sands.

In accordance with Polish legal regulations (the Journal of Laws of 1995 no. 16 item 78 with later amendments) such mining lands need to be reclaimed. Selection of an individual reclamation type to a considerable extent depends on physical and chemical properties of this heterogeneous material (Feng et al., 2019). Reconstruction of soil is the primary pre-condition for the development of new ecosystems in post-mining areas. Such locations provide valuable material for studies on the rate and duration of soil formation processes (Abakumov et al., 2013; Frouz et al., 2008). Those authors also reported that both the composition of the parent material and climate have a considerable effect on the intensity of soil formation processes.

Soil development is determined by the amount and quality of organic matter accumulated in the course of the reclamation process (Abakumov et al., 2013). In turn, the amount and quality of organic matter are dependent on the applied reclamation
treatments, first of all the species of introduced plants and cultivated treatments (Bender, 1995; Pietrzykowski and Krzaklewski, 2010; Gilewska and Otremba, 2018). These factors are also crucial for the development of chemical properties in newly formed soils (Pająk and Krzaklewski, 2006). Assessment of these properties, along with physical and biological properties provides important indications of pedological processes (Mukhopadhyay et al., 2016).

The aim of the study was to assess chemical properties of soils developing under the impact of their agricultural reclamation. This paper presents an analysis of the effect of three mineral fertilisation variants in the cultivation of Medicago sativa L. on accumulation of carbon and major nutrients as well as sorption properties of young soils.

2. Materials and methods

Study site

Investigations were conducted in a post-mining area of the former Pątnów strip lignite mine in the Konin–Turek Lignite Basin near the city of Konin (52°18′41.13″N, 18°15′39.19″E). The experimental field of 20 ha was established in 1978. Results presented in this paper are the effect of agricultural reclamation performed following the concept (PAN model of the Polish Academy of Science) developed by Bender (1995). This study was conducted on 3 experimental sites. In each site a different mineral fertilisation variant was introduced: ONPK (no fertilisation), 1NPK (160 kg ha⁻¹ year⁻¹ N, 40 kg ha⁻¹ year⁻¹ P₂O₅, 80 kg ha⁻¹ year⁻¹ K₂O) and 2NPK (320 kg ha⁻¹ year⁻¹ N, 80 kg ha⁻¹ year⁻¹ P₂O₅, 160 kg K₂O ha⁻¹ year⁻¹). Potassium-phosphorus fertilisation was applied in one dose (ammonium nitrate). The cultivated crop was a monoculture of alfalfa (Medicago sativa L.) with a 10% addition of orchard grass (Dactylis glomerata L.). From the beginning of the experiment these crops were replanted several times. Alfalfa biomass was harvested annually, three or four times a year, with total yields of 15–40 t ha⁻¹ year⁻¹ for the ONPK variant, 24–60 for 1NPK and 29–85 t ha⁻¹ year⁻¹ green mass in the 2NPK variant.

Sampling and analyses

In 2019 in each of the three experimental plots (ONPK, 1NPK and 2NPK) two soil profiles were made to reveal soil morphology. In each case two genetic horizons were distinguished (Ap and C). Each of these horizons was divided into two subhorizons Ap1 and Ap2 as well as C1 and C2. The thickness of the Ap1 subhorizon ranged from 10 to 12 cm, while that of Ap2 ranged from 12.5 to 15.5 cm. Altogether the thickness of both Ap subhorizons ranged from 24 to 26 cm. From each of the distinguished subhorizon soil samples with a disturbed structure were collected. Air dry soil samples were screened using sieves with 2 mm mesh size diameter. Such prepared samples constituted material for laboratory analyses. The grain size distribution was analysed applying a combination of the hydrometer and the wet-sieve methods (ISO 11277, 2009). The division into texture classes followed the USDA recommendations (Schoeneberger et al., 2012). The sand fraction content ranged from 63 to 70%, the amount of silt within the range of 22–28%, while that of the clay fraction was 8–11%. Irrespective of the soil horizon and fertilisation variant the analysed soils were classified as Spolic Technosols, according to the IUSS Working Group WRB (2015) with texture of fine sandy loam (FLS). The total nitrogen content (TN) in the soil was determined according to Kiejdahl (ISO 11261, 1995). Total carbon content (TC) in the soil was assayed by dry incineration using a Multi N/C 3100 Analytikjena apparatus. Carbonate content (CaCO₃) was estimated applying Scheibler’s volumetric method. Based on TC and carbonate contents the soil organic carbon (SOC) content was calculated from the formula SOC = TC – (0.12×CaCO₃). The content of available magnesium (Mg) was assayed using the Schachtschabel methods, while available forms of phosphorus (P₂O₅) and potassium (K₂O) – according to Egner–Riehm. Soil pH was determined using the potentiometric method in 1 mol·dm⁻³ KCl at the soil:solution ratio of 1:2.5 (v:v). Total exchangeable bases (TEB) in soil were assayed using the Mehlich method as modified by Kociakowska and Ratajczak (1984), while acidity (H⁺) was determined in 1 mol dm⁻³ CH₃COONa at pH 8.2. Their sum constituted total cation exchange capacity (CEC). For each collected soil sample the analyses were performed in 3 replications.

Statistical analysis

Statistical analyses were performed using the Statistica 13.0 program (StatSoft, Inc., USA) and MS Excel software. Significance of differences in chemical properties between the means of the soil subhorizons at individual fertilisation doses, as well as between subhorizons of various fertilisation doses were determined using Tukey’s test at α = 0.05. The differences were considered significant at p ≤ 0.05. Correlation coefficients between selected soil properties were calculated using Pearson’s test.

3. Results and discussion

Analysed soils were characterised by relatively similar reaction. The pH values ranged from 6.94 to 7.69 (Fig. 1). The basic soil reaction was caused by the presence of calcium carbonates (Fig. 2). Calcium carbonates were distributed throughout the entire profile of the analysed soils. Their contents didn’t depend on the fertilisation dose and it was varied. The highest calcium carbonate content was found in the Ap1 and C2 subhorizons of the 2NPK variant (59.7 and 60.9 g kg⁻¹) and the C1 subhorizon in the ONPK variant (64.5 g kg⁻¹). Significantly lower contents were recorded in the Ap1 and Ap2 subhorizons of the control and 1NPK variants (from 42.4 to 43.9). The lowest level of carbonates was recorded in the C2 subhorizon in the 1NPK variant (40.3 g kg⁻¹) (Fig. 2). Varied amounts of CaCO₃ resulted from the specific distribution of the abundant rock in those sites and those less abundant in that compound in the parent material. Calcium carbonate content depends on the
The most variable characteristics of the post-mining area in the Wielkopolska region (Gilewska and Otremba, 2002). The presence of calcium carbonates and the basic soil reaction are also typical of soils developing from that parent material (Gilewska and Otremba, 2004, 2018). The basic reaction is also reported in German dumps composed of loess (Pihlap et al., 2019).

The level of total carbon (Fig. 3) fell within a wide range of values. In subhorizons Ap1 and Ap2 the TC level was 17.4–21.0 g kg⁻¹ for 0NPK, 19.3–22.4 g kg⁻¹ for 1NPK and 23.8–26.7 g kg⁻¹ for 2NPK. The TC pool is composed of soil organic carbon (SOC) and inorganic carbon bound with carbonate minerals. As it results from our studies, subhorizons C1 and C2 were charac-
terised by 1.5 to 2-fold lower TC content compared to its level in the surface soil horizons. Our results indicate a marked TC accumulation in the Ap horizon. The presence of calcium carbonates in the soil profile increased the TC pool in the analysed soil (Figs. 3 and 4), although no statistically significant correlation of TC with CaCO₃ content or pH was found. The TC content showed the strongest correlation with SOC (r = 0.98) (Table 1).

The content of soil organic carbon (SOC) in surface subhorizons Ap1 and Ap2 increased statistically significantly with an increasing fertilisation dose, reaching a maximum in the 2NPK variant (19.5 and 18.2 g kg⁻¹) (Fig. 4). In the subhorizons of the parent material (C1 and C2) the SOC content was considerably less varied and ranged from 6.10 to 9.09 g kg⁻¹ (Fig. 4). Thus they were the levels from 2 to 3-fold lower than in the Ap horizons. It needs to
be stressed that in the SOC pool in the post-mining areas not only pedogenic carbon is found, but also geogenic carbon related with the presence of lignite (Greinert et al., 2018). Such a situation was typical of the parent material horizons in the analysed soils. In those horizons not only small lignite crumbs were found, but also reside of thick alfalfa roots. In Ap no lignite particles were observed, which indicates that these horizons contain primarily pedogenic carbon. A significantly greater SOC accumulation in the Ap horizons in the 1NPK and 2NPK variants (14.1–19.5 g kg⁻¹) compared to 0NPK (12.1–15.9 g kg⁻¹) was caused, as it may be assumed, by the greater influx of organic compounds, since fertilisation influenced yields of plants, as mentioned above. The yields were greatest for 2NPK and lowest in the case of 0NPK. Greater yields are also connected with greater amounts of plant residue in mining soils. The SOC levels recorded in this study for all the fertilisation variants need to be considered high compared to the mean SOC content in Polish cultivated mineral soils. Siebelec et al. (2017) reported that in 2015 this value was 11.2 g kg⁻¹.

Presented results are characteristic of processes observed in the initial stages of soil formation. Reintam et al. (2002), Fet-tweis et al. (2005) and Pihlap et al. (2019) indicated that the accumulation and humification of organic matter play the main role in the initial soil formation stages. The soil organic matter (humus) serves a key role in the modification of soil properties not only in reclaimed areas (Vindušková and Frouz, 2013; Zhao et al., 2013; Bao et al., 2017; Ahirwal et al., 2018), but also in arable soils (Chaudhari et al., 2013; Scotti et al., 2015). Humus is a significant link in the cycle of mineral nutrition of plants and soil organisms by storing and enhancing the availability of nutrients, mainly nitrogen and phosphorus (Stevenson, 1994; Frouz et al., 2008; Pietrzykowski, 2010). Presented results indicate that despite the passage of over 40 years since the initiation of soil formation, the analysed Technosols still show a clear carbon sequestration. This process has also been highlighted by Ahirwal et al. (2018) and Mukhopadhyay et al. (2016). Our results indicate that SOC is positively correlated with all determined properties (except for pH and CaCO₃). Values of the correlation coefficient for SOC with TN need to be stressed in this respect (r = 0.97), CEC (r = 0.90), Ca²⁺ (r=0.89), K₂O (r = 0.85) P₂O₅ (r = 0.83) (Table 1).

Nitrogen is a macronutrient, which determines not only the amount of biomass produced in the course of the reclamation processes, but also the rate of soil formation processes and indirectly also soil structure formation processes (Bender, 1995; Gilewksa, 2000). In post-mining areas a deficit of this macronutrient is observed. For this reason in various reclamation technologies, irrespective of the adopted direction, nitrogen supply is focused on. It is provided by mineral fertilisation or introduction of legumes or other plants capable of fixing atmospheric nitrogen thanks to symbiosis with rhizosphere microorganisms (Fustec et al., 2010; Chodak et al., 2019; Pihlap et al., 2019). As it results from our study (Fig. 5), the TN levels in subhorizons Ap1 and Ap2 were statistically significantly greater than in the other analysed subhorizons. In the case of each fertilisation variant the Ap1 subhorizon was always characterised by significantly greater TN contents than Ap2. The fertilisation variant also had a significant effect on TN content. With an increased fertilisation dose the content of nitrogen in soils increased reaching a peak in subhorizon Ap1 in the 2NPK variant (3.17 g kg⁻¹). It needs to be stressed that TN content in the 1NPK and 2NPK variants is a consequence of a joint effect of mineral fertilisation and nitrogen fixation by Medicago sativa L. In turn, in the 0NPK variant (1.83–2.06 g kg⁻¹) the TN content results only from the effect of alfalfa (Medicago sativa L.). The 3- to 4-fold lower TN contents were found in the subhorizons of the parent material (C1 and C2), which indicates a marked accumulation of this macronutrient in the topsoil. The amount of TN in soil subhorizons Ap in all fertilisation variants fell within the upper limit of values given by Siebielec et. al. (2017) for arable soils in Poland (0.4–3.6 g kg⁻¹). In relation to the mean values in arable soils (1.12 g kg⁻¹) reported by the above-mentioned authors, the amount of TN in the Ap soil horizon in the control variant was almost 2-fold and in the 2 NPK variant was as much as 3-fold greater.

It results from the data given in Table 1 that the amount of TN, similarly as SOC, is positively correlated with all the determined properties except for pH and CaCO₃. Accumulation of TN resulted not only in the increased levels of total nitrogen, but also reduction of the SOC:TN ratio (Fig. 6). In subhorizons Ap1 and Ap2 this ratio ranged from 6.14 to 7.7. Such a narrow value

![Fig. 5. Mean contents of total nitrogen in soil subhorizons depending on fertilisation variant. Different letters indicate significant differences (p ≤ 0.05) according to Tuckey test](image-url)
of the SOC:TN ratio indicates a rapid rate of transformation of organic matter introduced to the formed soil. In the parent material horizons the SOC:TN ratio fell with a wider range of values from 8.2 to 16.1. The smallest range of the SOC:TN ratio in the parent material horizons was recorded in the 2NPK fertilisation variant, in which every year 320 kg N ha⁻¹ were introduced, while it was widest for 0NPK. Nitrogen fertilisation in alfalfa growing may have limited the development of Rhizobium and Bradyrhizobium bacteria, and thus reduced the capacity to fix molecular nitrogen. The inhibitory effect of mineral nitrogen consists in the limitation of development of root nodule biomass and a reduction of nitrogenase enzymatic activity (Gaweł, 2011).

In view of the above at the current stage of the research it seems that nitrogen fertilisation in alfalfa cultivation in post-mining areas may not be required.

Apart from nitrogen another deficient macronutrient in post-mining areas is phosphorus (Pietrzykowski and Krzaklewski, 2010; Zoubková et al., 2015). Previous studies (Gilewska, 2000; Gilewska and Otrzemba, 2004) indicated a rapid accumulation of available phosphorus forms in soils developing in post-mining areas. This is also confirmed by the present study (Fig. 7). The greatest contents of available phosphorus forms were found in the topsoil subhorizons: Ap1 (206.9 mg kg⁻¹) and Ap2 (124.4 mg kg⁻¹) in the 2NPK variant. Contents over 201 mg kg⁻¹ P₂O₅ in arable soils are considered very high. The amount of this macronutrient in the topsoil horizons decreased significantly as follows: 2NPK>1NPK>0NPK. In the 1NPK variant the content of P₂O₅ was between low and medium. In subhorizon Ap1 – 0NPK a low value was recorded, but it was a statistically significant and greater (almost 2-fold) content of phosphorus than in the deeper soil subhorizons. This indicates a slow process of accumulation of this element under the influence of cultivated crops (Medicago sativa L.). The alfalfa plant mass, as reported by Gawel (2011), is abundant in nutrients, among other phosphorus. It may be assumed that biomass entering the soil and undergoing decomposition processes results an enrichment of subhorizon Ap1 with this macronutrient. These studies showed no statistically significant correlation for contents of available phosphorus forms only with CaCO₃ contents. In contrast, statistically significant correlations were observed with all the other parameters. Compared to the mean content of available phosphorus forms in Polish mineral soils (154 mg kg⁻¹) reported by Siebielec et. al. (2017) in the Ap horizon in the 0NPK variant the levels of this macronutrient are approx. 3-fold lower, in the 1NPK variant 2-fold, while in the 2NPK variant they exceed the mean.
Moreover, significant differences were also observed in contents of available potassium (Fig. 8) both between the soil horizons and in the fertilisation variants. Content of this macronutrient was very low in subhorizons Ap1 and Ap2 in the 0NPK variant as well as C1 and C2 for all the fertilisation variants, whereas it was medium in the Ap horizon at 2NPK. It needs to be added here that despite marked differences in contents of available potassium forms in the analysed soils they were even lower than the mean in arable soils (Siebielec et al., 2017). Content of potassium in the soils investigated in our study may be partly modified by its presence in minerals such as smectite and illite. Presence of these minerals was confirmed by earlier studies (Otremba and Gilewska, 2013). A very strong positive correlation of P2O5 and K2O contents needs to be stressed here (r = 0.91), as it indicates that both macronutrients are strongly dependent on the applied mineral fertilisation variant (Table 1).

Data presented in Fig. 9 concerning contents of available magnesium show considerable abundance of soils formed in post-mining areas in terms of content of this macronutrient. As it results from the study, the greatest content of available Mg forms was recorded for subhorizon Ap1, particularly in the 0NPK and 2NPK variants (81.7 mg kg⁻¹ and 88.0 mg kg⁻¹, respectively). We also need to stress high contents of available Mg also in the other soil subhorizons (from 50.3 to 72.8 mg kg⁻¹) compared to arable soils in Poland (1–32 mg kg⁻¹) (Siebielec et al., 2017). Such results indicate that the amount of magnesium in the soil developing in post-mining areas is determined first of all by its content in overburden rocks, i.e. it is of geogenic origin. Zoubková et al. (2015) and Frouz et al. (2011) pointed to high contents of magnesium in Czech post-mining areas composed of Miocene clays.

The CEC values in the analysed soils ranged from 7.45 to 13.16 cmol kg⁻¹. These are values exceeding the mean cation exchange capacity (6.51 cmol kg⁻¹) of arable soils in Poland (Siebielec et al., 2017). The highest cation exchange capacity was found for topsoil subhorizons Ap1 and Ap2 (10.14–13.16 cmol kg⁻¹). It needs to be stressed here that these values increased significantly with an increase in the fertilisation dose. This was probably caused by the increasing SOC. An increase in SOC resulted in a greater amount of organic colloids and these in turn contributed to an increased CEC in soil. Compared to the Ap horizon the CEC values in subhorizons C1 and C2 were by 2–4 cmol·kg⁻¹ lower. The high CEC value in these subhorizons resulted first of all from the presence of illite and smectite in the colloid clay fraction of the analysed soils, as reported by Otremba and Gilewska (2013) (Fig. 10A). Additionally, the presence of iron and aluminium oxides may not be excluded here. The
considerable effect of the above-mentioned properties on CEC in arable soils was reported by (Asadu et al., 1997; Morrás, 1995; Soares et al., 2005). Those authors added that a marked role in the modification of CEC in soil is played by the origin and properties of the parent rock (its mineral composition, susceptibility to weathering), pedogenic processes and climatic conditions (affecting the intensity of weathering processes). Moreover, it also results from our analyses that the Ca\(^{2+}\) cation accounted for 83% cation exchange capacity. The share of calcium in CEC, as shown in Fig. 10B, particularly in subhorizon Ap1 increased from 85% in the soil of the 0NPK variant to 87.2% in 2NPK. This may have been caused by partial extraction of calcium from carbonates during assays of basic cations (Brogowski and Chojnicki, 2019).

Those authors extensively described the role of calcium in the modification of CEC in arable soils developing from glacial tills. As it was reported by those authors, the formation of active carbonates is a major process in chemical weathering. The varied influx of organic matter to the Ap horizons, a greater pool of hydrogen ions as well as variable moisture conditions may facilitate the formation of active carbonates, from which Ca is the most readily leached element. Obtained results and the high correlation coefficient between Ca\(^{2+}\) and H\(_{exc}\) (r = 0.85) may indicate that the level of fertilisation through the amount of organic matter reaching the soil influences the intensity of weathering processes (Table 1).

The amount of potassium in CEC decreases with increasing fertilisation doses. This may be associated with the reversal process of this macronutrient. This process under conditions found in soils developing in post-mining areas in the Wielkopolska region was reported by Gilewska (2000). The shares of individual components in CEC decreased in the following order Ca\(^{2+}\) → Mg\(^{2+}\) → H\(^+\) = K\(^+\) → Na\(^+\) (Fig. 10B).

5. Conclusions

The obtained results indicate that irrespective of the applied fertilisation variant cultivation of Medicago sativa L. had a significant effect on changes in the chemical properties of soils developing in the Pątnów spoil bank in the Konin–Turek Lignite
Basin. The observed effects were manifested in the statistically significant increase in SOC and TN contents as well as CEC in topsoil subhorizons Ap1 and Ap2 in the 0NPK variant (no mineral fertilisation). Mineral fertilisation (1NPK and 2NPK) additionally intensified changes in these chemical properties, while it also caused an accumulation of contents of available phosphorus and potassium forms.

The results indicate that mineral fertilisation probably stimulates also Ca\(^{2+}\) leaching from carbonates. However, it may be assumed to be an indirect effect through the increased penetration of organic matter to the soil.

Among the recorded properties, the analysed soils retain the following features from the parent material: the basic reaction, the presence of calcium carbonates, high contents of available magnesium and relatively high CEC value.

The recorded high TN content and a narrow range of the SOC:TN ratio in the case of all the fertilisation variants indicate the potential elimination of nitrogen fertilisation in alfalfa culture in post-mining areas. This is because it may reduce fixing of atmospheric nitrogen by *Medicago sativa* L.

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Właściwości chemiczne Technosoli na terenach pogórniczych

Końko-Tureckiego Zagłębienia Węgla Brunatnego

Słowa kluczowe

Tereny pogórnicze węgla brunatnego
Rekultywacja rolnicza
Medicago sativa L.
Właściwości chemiczne gleb
Węgiel organiczny

Streszczenie