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Methods for calculating carbon sequestration in degraded soil of zinc smelter and post-mining areas

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ABSTRACT

Land degradation is one of the fundamental problems in the world. To counteract soil degradation processes, many remedial actions consisting of improving soil physical and chemical properties, restoration of the soil humus, and restoration of plant cover are taken. This greenhouse experiment combined process of carbon sequestration and phytoremediation of degraded soils. The main aim of the study was to indicate the best method of calculation of carbon storage based on the level of organic matter, humic acids, different types of carbon (total carbon [TC], total organic carbon [TOC], dissolved organic carbon, etc.) and indicators of soil carbon sequestration. A series of indexes, including carbon management index (CMI), SOC pool, C stock, C sequestration rate, SOC build up rate, were calculated to estimate carbon storage in soils affected by zinc smelting and mining activities. Several minerals(i) accompanying brown coal deposits (lacustrine chalk) and (ii) coal slurry were used as soil amendments. Moreover the organic wastes compost and sewage sludge were also used. Under the influence of these substances, especially municipal compost, lacustrine chalk and coal slurry, the improvement of soil fertility and soil quality was observed, based on changes in the basic parameters of the soil (total Kjeldahl nitrogen, TC, TOC). Phytoremediation process was carried out by using giant miscanthus (*Miscanthus × giganteus*) and scots pine (*Pinus sylvestris* L.). The plant application, especially pine trees, contributed to the soil organic carbon sequestration and storage. As the most useful fertilizer additives were considered lacustrine chalk and coal sludge. The CMI and SOC sequestration rate were the best methods to determine carbon sequestration in the soil during conducted pot experiment.

Keywords: Carbon sequestration; phytoremediation, degraded soils; Carbon management index; Soil carbon pool; Soil organic carbon build up

1. Introduction

The observed processes of soil erosion, land degradation and soil devastation are associated with natural phenomena that occur on earth, but to a large extent is the consequence of human and industrial activities. It is estimated that approximately 50,000 km^2 of globally land lose the utility value and about 24 billion tons of the level of humus as a result of soil degradation [1,2]. A significant decline in soil quality, due to accumulation of contaminants and the loss of organic matter, is also observed. Land degradation is associated with the emission of 20% carbon dioxide (CO_2)

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discharged into the atmosphere in recent years [3,4]. In addition, dewatering of peat, peatlands conversion and overexploitation of global peatlands contribute to emissions of 0.8 billion tonnes CO_2 per year [5]. The excessive CO_2 emissions can be substantially reduced through the rational management of the ground surface and also by properly planned and conducted land remediation of contaminated soils [6,7].

Excessive concentration of CO_2 in the atmosphere and the loss of carbon from the soil are important environmental problems which are correlated with each other. In order to minimize the intensity of the greenhouse effect and the loss of large amounts of organic matter from the soil environment, carbon sequestration and management is one of the most important activity [8–10].

Carbon sequestration can be defined as the totality of promote measures to reduce and stabilize the level of carbon dioxide in the atmosphere. Carbon sequestration involves primarily capture and uptake of CO_2 from the air and then immobilization and storage of this gas by using methods: physical (e.g., geological storage in the oceans), chemical (e.g., mineral carbonation technology) and biological (e.g., reforestation, ecological agriculture, phytoremediation) [6,11–15]. Biological carbon sequestration includes preventing excessive emissions of CO_2 from the soil through rational management and use of the soil environment, afforestation, reduced plowing, judicious use of mineral fertilizers in agriculture, the use of phytoremediation for reclamation of contaminated and degraded soils and appropriate selection of crop species (e.g., energy crop and forest species) [16–25].

Biological methods are based on a carbon phytosequestration, which consists of reduced CO_2 emission due to the uptake of CO_2 by plants during photosynthesis, then carbon stored in plant tissues and finally the plant decomposition, decaying and humification of organic matter in the soil.

Carbon sequestration is often considered as the side effect of phytoremediation of soils. These processes, however, are closely interrelated [24]. Improving soil quality and plants restoration in degraded areas can reduce greenhouse gas (including CO_2) emissions by soil-binding plants [25–29]. Furthermore, fertilization of degraded soils is able to produce higher yields (biomass) and thereby absorb more amount of CO_2 by plants and enable larger amount of carbon in plant tissue [30]. Therefore, appropriately planned phytoremediation process, including more efficient process of carbon sequestration in soil and phytosequestration of this element in plants, has many advantages. To the positive aspects of the combination of these two processes may be also included the following: versatile application in relation to the different types of soil, a small financial outlays, an insignificant interference in the natural environment, the ability to recover some of the costs (e.g., through the sale of wood, biomass energy, compost). An additional advantage is the possibility of using wastes as fertilizers to promote the plant growth and to improve the soil quality [31–33].

This experiment involved a combined process of carbon sequestration and phytoremediation of degraded soils. The aim was to estimate the carbon storage based on the level of organic matter, humic acids, different types of carbon (total carbon [TC], total organic carbon [TOC], dissolved organic carbon [DOC], etc.) and different indicators of soil carbon sequestration. In the pot experiment, two degraded soils, fertilized with different organic and mineral additives were compared. Phytoremediation process was carried out by using giant miscanthus (*Miscanthus* × *giganteus*) and scots pine (*Pinus sylvestris* L.).

2. Material and methods

2.1. Characteristic of degraded soils

Soil materials for pot experiment from two different degraded areas were used. The first soil samples (200 kg) were obtained from an area affected by a zinc smelter (ZS) in Silesia (50°30′27.1″N 18°56′09″E). Soil samples from this area are characterized by a high concentration of heavy metals, especially zinc, cadmium, lead and with low pH, and low sorption capacity. The soil is a sandy with poor biogenic elements and organic matter (Table 1). The second set of soil samples (200 kg) was collected from brown coal post-mining area (CM) (51°15′54″N 19°4′41″E) with loamy sand mining output from different excavation levels. This soil has a lower fertility and did not have a proper soil profile development due to mining activities and strong mechanical degradation. Soil samples were collected from the surface of opencast mine placed on an external dump. Soil from the dump was characterized by poor soil structure and deterioration of soil quality (loss of humus in soil), but at the same time the soil exhibited biological activity. In this area soil-forming processes and accidental vegetation were also observed. Soil samples have high pH and low moisture content. This soil has also low biogenic element, organic material content and low concentration of heavy metals (Table 1).

2.2. Characteristic of soil additives

Organic and inorganic substances were used in the pot experiment to investigate the improvement of carbon content and carbon sequestration in soils. Four soil amendments: sewage sludge (Ss – sewage sludge, 15 Mg/ha calculated on volume of pots with plants) from food industry, compost (Co – compost, 15 Mg/ha calculated on volume of pots with plants) from the biodegradable fraction of municipal waste, coal slurry (Cs – coal slurry, 2 wt% of soil in pot) from coal preparation plant and lacustrine chalk (Lc – lacustrine chalk, 2 wt% of soil in pot) from a brown coal mine were used. Sewage sludge and compost were used to enrich the degraded soils with biogenic elements and organic matter,

Table 1
Soil chemical characteristics

Parameter	Zn smelter soil	Brown coal mining area soil
pH (H_2O)	5.5 ± 0.1	8.1 ± 0.1
CEC (cmol(+)/kg dm)	3.2 ± 0.1	23.9 ± 0.2
C total (g/kg dm)	12.9 ± 0.1	4.1 ± 0.1
N Kjeldahl (mg/kg dm)	577 ± 18	108 ± 123
P total (mg/kg dm)	176 ± 1	132 ± 1
Zn (mg/kg dm)	1,750 ± 57	15 ± 1
Cd (mg/kg dm)	28.8 ± 1.2	0.4 ± 0.1
Pb (mg/kg dm)	1,700 ± 87	5 ± 1

coal slurry and lake chalk to reduce the mobility of heavy metals. The soil additives were characterized by a high nutrient content and low concentration of heavy metals and PAHs (Table 2).

2.3. Experimental plan

The pot experiment was carried out under controlled conditions in a phytotron chamber over a period of 18 months. The experiment was held at a constant temperature of 21°C/18°C (day/night), with relative humidity ranging between 60%–90%. Soils were mixed with the four inorganic and organic amendments (Table 2) and placed in pots (with 5 kg of mixtures) with three replications. The pots were watered prior to the planting of giant miscanthus (*Miscanthus × giganteus*) and scots pine (*Pinus sylvestris* L.). The three individual seedlings were planted in each of three pots with the same mixture (three repetitions per one combination, so nine individual plants per one combination). Pots without plants were kept as a control (Table 3). After termination of the experiment, soil samples were collected and analyzed for a series of physical–chemical parameters. At the beginning of the experiment, soil samples were also collected, which were reference samples.

2.4. Soil sampling and analysis

A preliminary analysis of soil samples taken from degraded areas and the mixtures was carried out. Soil samples from each pot were taken after the harvest of plants. Soil samples were air-dried and passed through a 2-mm mesh screen. The following parameters were measured for the soil samples collected:

- pH in deionized water suspension (ratio 1:2.5 soil to water). The pH was determined by the potentiometric method after 24 h incubation period (according to Polish Standard PN-ISO 10390:1997),
- Humic acids (HA) – concentration of humid acids measured after soil extraction in 0.1 M NaOH and 0.1 $Na_4P_2O_7$ (1:1 ratio). Soil solution mixtures were shaken for 5 min and incubated for 24 h. The supernatants were decanted, filtered through qualitative filter papers, acidified to pH = 1–1.5 with concentrated HCl and again incubated for 24 h. In the last stage of the analysis, the supernatants were filtered through quantitative filter papers and weighed [34],
- Loss on ignition (LOI) was method used to determine the soil organic matter content. The ignition of soil samples (5 g) took place in the muffle furnace at 500°C for 5 h [35],
- Total Kjeldahl nitrogen (TN) (according to Polish Standard PN-ISO 11261:2002) after mineralization with concentrated (95%) H_2SO_4 (using catalysts mixture of K_2SO_4 and Cu_2SO_4) and after alkalinization with 33% NaOH. In distillation and titration processes, 0.01 M HCl and 0.01 M NaOH were used due to the low N content in the soils.
- TC after dry combustion with using a Multi N/C H 1300 Analytik Jena analyser (according to Polish Standard PN-ISO 10694:2002),
- TOC using a modified Tiurin method – rapid dichromate oxidation techniques followed by colorimetric techniques (spectrophotometric determination) [36],
- DOC and particulate organic carbon (POC) – concentration of DOC and POC was measured after soil extraction in distilled water. Soil solution mixtures were shaken

Table 2
Characteristics of soil additives

Parameter	Sewage sludge	Compost	Coal slurry	Lacustrine chalk
pH (H_2O)	6.1 ± 0.1	6.9 ± 0.1	6.4 ± 0.1	7.3 ± 0.1
C total (g kg^{-1} dm)	401.1 ± 0.4	295.1 ± 6.2	364.1 ± 5.5	166.5 ± 4.7
N Kjeldahl (mg kg^{-1} dm)	39,670 ± 248	13,550 ± 149	16,770 ± 50	17,400 ± 50
P total (mg kg^{-1} dm)	5,200 ± 16	5,210 ± 15	131 ± 2	169 ± 2
Cd (mg kg^{-1} dm)	0.7 ± 0.1	1.4 ± 0.9	0.9 ± 0.1	0.4 ± 0.1
Pb (mg kg^{-1} dm)	6 ± 1	40 ± 3	38 ± 2	11 ± 1
Zn (mg kg^{-1} dm)	260 ± 11	453 ± 14	174 ± 11	23 ± 2
PAHs (µg kg^{-1} dm)	1,770 ± 23	5,100 ± 52	845 ± 41	1,340 ± 85

Table 3
Experimental plan of the pot experiment

Types of soil additives	Soil from the area of the zinc smelter			Soil from brown coal post-mining area		
	Pots with Scots pine	Pots with giant miscanthus	Control pots	Pots with scots pine	Pots with giant miscanthus	Control pots
Sewage sludge	X[a]	X	X	X	X	X
Compost	X	X	X	X	X	X
Coal sludge	X	-	X	-	-	-
Lake chalk	X	-	X	-	-	-

[a]X – mixture of soil and organic/inorganic amendments.

continuously for 24 h. The supernatants were decanted and filtered through qualitative filter papers (POC) and through cellulose syringe filters, 0.45 µm (DOC). A Multi N/C H1300 Analytik Jena analyser was used to determine supernatant DOC and POC [37],

- Soil bulk density (BD) was determined by weighing the sample in natural state, then dried soil sample in the glass measuring beaker of known volume. Bulk density of soil sample (Mg/m^3) was calculated = weight of soil (g)/volume of soil (cm^3) [38].

2.5. Carbon sequestration measurements

On the basis of the content of different carbon species and soil organic matter, the carbon indexes and carbon sequestration in soil were calculated by using the following equations:

The carbon management index (CMI) [39–41]:

$$CMI = CPI \times LI \times 100,\ \text{where}$$

CPI – the carbon pool index:

$$CPI = \frac{\text{total carbon pool in treatment sample } (g/kg)}{\text{total carbon pool in reference sample } (g/kg)};$$

LI – the lability index:

$$LI = \frac{\text{L in treatment sample } (g/L)}{\text{L in reference sample } (g/L)};$$

L – the carbon lability:

$$L = \frac{\text{content of labile carbon } (g/L)}{\text{content of non} - \text{labile carbon } (g/L)};$$

Reference sample was collected from the site of lignite mine dumping site (soil collection site for the pot experiment), collected after the experimental period.

The soil organic carbon (SOC) pool [38]:

$$SOC\ pool = SOC \times H \times BD \times 104 \times 10^{-2}\ (Mg/ha),$$

where SOC – soil organic carbon concentration (%); H – soil depth in the pot (m); BD – bulk density (Mg/m^3).

The carbon stock (C stock) [42]:

$$C\ stock = SOC \times H \times BD \times 10\ (Mg/ha)$$

where SOC – soil organic carbon concentration (g/kg), H – soil depth in the pot (m); BD – bulk density (g/cm^3);

The carbon sequestration rate (C sequestration) [42]:

$$SOC\ sequestration\ rate = SOC\ final - SOC\ initial \times H \times BD \times 10/T,\ (Mg/ha \times year),$$

where SOC final – soil organic carbon concentration at the end of the experiment (g/kg), SOC initial – soil organic carbon concentration at the beginning of the experiment (g/kg), H – soil depth in the pot (m); BD – bulk density (g/cm^3); T – time (year).

The soil organic carbon build up rate (SOC build up rate) [42]:

$$SOC\ build\ up\ rate = SOC\ treatment - SOC\ control \times H \times BD \times 10/T,\ (Mg/ha \times year),$$

where SOC treatment – soil organic carbon concentration in treatment soil samples (g/kg), SOC control – soil organic carbon concentration in control soil samples (g/kg), H – soil depth in the pot (m); BD – bulk density (g/cm^3).

2.6. Statistical analysis

Results obtained are expressed as means with standard errors. Differences between means were determined by one-way analysis of variance (ANOVA) and Tukey's honest significant difference test at $p < 0.05$. Furthermore, the correlations between selected methods used to calculate soil carbon sequestration (SOC pool and SOC stock, SOC build up rate and CMI, SOC build up rate and C sequestration rate) were analyzed and were expressed as the coefficient of determination R2 and the linear regression (Figs. 5–7).

3. Results and discussion

3.1. Changes in the content of soil organic matter, different carbon species and humic acids in soils

Soil organic matter content and the content of different form of carbon and humic acids in degraded soil and post-mining land are good indicators of soil quality. High content of these soil properties show high soil fertility and plant nutrients. For this reason some soil properties, such as TC, TOC, POC, DOC, LOI and HA, may be also indicators of soil carbon input and stock. Fig. 1 shows the impact of organic and inorganic substances and plant grown on pH, TN, LOI, TOC, TC, POC, DOC and HA in the two degraded soils.

The phytoremediation process of degraded soil and post-mining land has improved some soil properties (e.g., TC, TN, TOC content) and small changes in soils pH were noted. Additionally, the process of carbon sequestration in two soils was noted, indirectly determined on the basis of changes in the HA and LOI content (Fig. 1). Analyzing the change of pH value in investigated soils, a slight increase in pH after application of compost and lacustrine chalk, and a slight decrease after sewage sludge and coal slurry application was noted (Fig. 1(A)). Similar fluctuations in soil pH after application of sewage sludge in degraded soils were noted by Placek et al. [43]. Furthermore, a similar change in soil pH after application of compost was obtained by Ouédraogo [44]. Lacustrine chalk is known to increase the soil pH due to its high content of carbonate. The application of pine and miscanthus plants also resulted in a small increase in the pH value of the two soils. This phenomenon can be explained by the effects of plant root exudates. Root exudates from soil-grown plants contain organic acid components (e.g., citric acid) and therefore decrease soils pH [45].

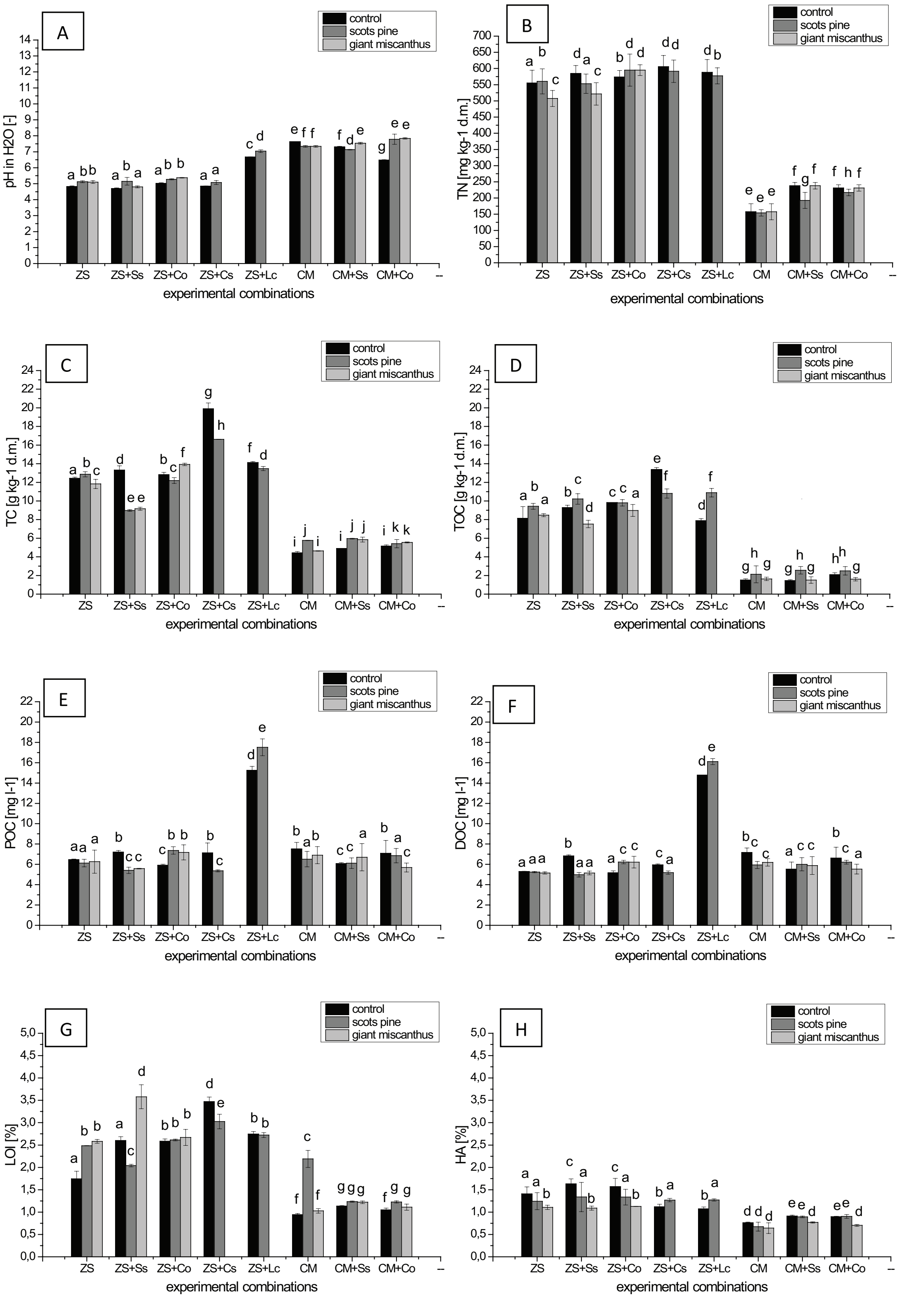

Fig. 1. Changes in pH (A), TN (B), TC (C), TOC (D), POC (E), DOC (F), LOI (G) and HA (H) content in two types of degraded soils. The letter combinations on X axis stand for ZS – zinc smelter soil, CM – brown coal mine soil, Ss – sewage sludge, Co – municipal compost, Cs – coal slurry, Lc – lacustrine chalk. Values are means with standard errors shown by the vertical bars (n = 2–3). Bars with the same letter(s) are not significantly different at $p \leq 0.05$.

Good indicators controlling the course of the two mentioned processes (carbon sequestration and phytoremediation of degraded soils) are TC, TN and TOC. All these parameters indicate the soil health [46]. In addition, carbon and nitrogen content in the soil can indicate the rate of decomposition or humification of organic matter involving soil bacteria. The application of fresh organic matter to soil is an important ecological process, which determines soil carbon storage and nutrient cycling [47–49]. Based on the results obtained in the pot experiment, it can be stated that municipal compost, coal slurry and lacustrine chalk can be a good source of biogenic elements (especially N total and C total) in the degraded soils. The fact that, wastes may be important sources of carbon and nitrogen for soils as confirmed by Kabore et al. [50] and Fabrizio et al. [51]. The results obtained by Steinbeiss et al. [52] show a slight increase of carbon after compost application. Only after the application of lacustrine chalk, a significant increase in the content of TC and TOC in the investigated soils was observed (Figs. 1(C) and (D)). This soil amendment, due its origin (minerals accompanying brown coal deposits), contains high content of organic and inorganic carbon. A similar effect of increased soil organic carbon content after the application of organic-mineral amendments was also obtained in other studies [42]. The long-term fertilization experiment on two soils, conducted by Yan et al. [41] consisted of nine treatments. Soils differed in the content of TOC, but a similar carbon fertilization effect was obtained. In these cases, soils contained increased TOC content under the application of chemical fertilizers and organic manure.

By measuring the concentration of POC and DOC in soil solution, it can determine the degree of leaching and loss of soluble organic matter from the soil [53]. In our experiment, the application of additives fertilizer did not cause a significant increase of TOC contents in soils, and therefore the degree of dissolved carbon leaching from soils was limited (Figs. 1(E) and (F)). A similar correlation between TOC and DOC was noted by Zhang [54] and Huang et al. [55]. The difference between the POC and DOC was very small. In addition, the concentration of DOC leaching had no significant impact neither by the application of soil additives, nor the introduction of plants. Only the application of lacustrine chalk, to soil from the zinc smelter area, increased the concentration of POC and DOC in soil solution. This phenomenon may be associated with high concentration of dissolved inorganic carbon, in comparison with another amendments, of this soil additive. Whereas, the high concentration of POC and DOC in brown coal mine soil could be also associated with a high clay fraction in this soil.

In turn, the amount of organic matter and the degree of its sequestration in the soil can be also determined on the basis of LOI and the amount of HA in investigated soils. The more efficient humification of organic matter encourages carbon sequestration in the soil. In the pot experiment, the application of virtually all fertility additions to the zinc smelter soil increased the organic matter content. However, only a small part of the applied organic matter was undergone the process of humification in soils (Figs. 1(G) and (H)). Organic matter derived from sewage sludge and municipal compost has undergone humification process and caused an increase in HA content in both soils. Whereas, the application of coal slurry and lacustrine chalk did not contribute to soil organic matter storage determined based on the HA content. A big influence on the humification of organic matter was observed after the application of two plants, which reduced the content of soil organic matter and analogously impeded the process of humification. Plant root secretions may have contributed to the rapid decomposition of organic matter and release of valuable nutrients, necessary for plants for proper growth and development [56]. This phenomenon was more evident in the case of miscanthus.

Both soils were poor in biogenic elements, especially the soil from post-mining land due to its origin. Leaching of DOC was determined on the basis of the contents of POC and DOC. After completion of the pot experiment, it can be presumed that more amount of organic matter, applied through soil additives, was aerobically oxidized or decomposed due to plant activity, than was leaching into lower layers. The decrease of DOC with organic matter (coming from sewage sludge) mineralization confirms research conducted by Fang et al. [57]. It is difficult to determine the impact of the introduction of two plant species to degraded soils because of short duration. There were no significant differences in the analyzed parameters in pots with pine and miscanthus. Only on the basis of the humic acids content, it may be presumed that giant miscanthus, due to its large biomass in the initial stage of growth and high demand for biogenic elements, contributed to a more rapid decomposition of soil organic matter.

Soil characteristics give basic data for the calculation of some carbon stock indexes and carbon management index to determine soil carbon sequestration.

3.2. Changes in CMI value for degraded soil and post-mining land

The carbon management index (CMI) is a crucial indicator of carbon transformations in soil, which shows the relationship occurring between the concentration of total carbon, carbon labile and non-labile carbon. CMI was calculated based on the values of CPI and LI [41]. By using this index, the effect of the annual carbon addition, through the introduction of organic-inorganic soil additives, and the impact of the plant cultivation during the short-term pot experiment was estimated (Fig. 2).

Higher CMI values in zinc smelter soil than in soil collected from coal mine land were recorded (Fig. 2). This result is strongly correlated with the soil quality and parameters. Soil from smelter area showed a higher content of different types of carbon (Figs. 1(C) and (D)). Similarly the application of different fertilizer additives affected the higher CMI values. The highest values of this parameter were noted after the application of municipal compost and lake chalk. A similar effect of soil fertilization on CMI was obtained by Verma et al. [58] and Zhu et al. [59]. Higher application of carbon resulted into higher CMI values. A similar phenomenon was observed for changes in TN content in soils and changes in the CMI value (Figs. 1(B) and 2). Similar conclusions were drawn by Vieira et al. [41] and Blair et al. [60]. In these studies organo-mineral fertilization promoted significant increase in the content of TC and TN, and thereby higher CMI values. Thus, both of the C content and also the N content in the soil can affect the CMI values. At the same time, a tendency to considerable leaching of some soil amendments, for example, sewage sludge, was observed. The phenomenon of leaching of sewage sludge into lower layers (some leachate came out of the pots through pot perforation) can also be presumed on the basis of the reduction of total carbon content obtained at the end of the experiment (Fig. 1(C)).

The impact of plant cultivation on CMI value was also analyzed. In some cases, the introduction of both of the two plant species contributed to a slight increase in CMI. In addition, a higher of CMI value was noted in pots with pine trees (Fig. 2). This plant characterized by a highly branched root system, which hinders the carbon losses from soil. Whereby cultivation of pine trees can prevents the mineralization of organic matter and carbon leaching into the soil profile, thus promotes soil carbon storage. Similar results were obtained by Richards et al. [61].

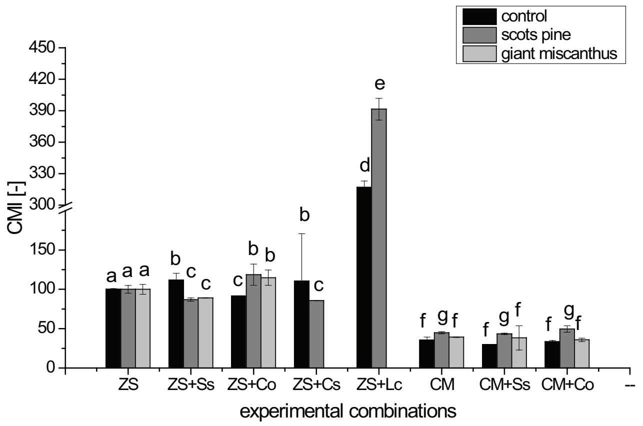

Fig. 2. Changes of CMI value in two types of degraded soils. The letter combinations on X axis stand for ZS – zinc smelter soil, CM – brown coal mine soil, Ss – sewage sludge, Co – municipal compost, Cs – coal slurry, Lc – lacustrine chalk. Values are means with standard errors shown by the vertical bars (n = 2–3). Bars with the same letter(s) are not significantly different at $p \leq 0.05$.

3.3. Changes in soil organic carbon pool and carbon stock in two soils

The SOC pool and C stock are analogous methods used in determining soil carbon accumulation at the end of pot experiment. Both methods take into account soil organic carbon concentration, soil depth and bulk density [38,42]. The application of organic-mineral soil amendments and plant grown in varying degrees influenced on soil organic carbon pool (Fig. 3(A)) and carbon stock (Fig. 3(B)).

High values of both indexes were reported (Fig. 3). Both soils were poor in organic matter content (Fig. 1(G)). However, the application of fertilizer additives improved the soils quality and its organic matter content significantly. Therefore, low carbon input values and low concentration of carbon in reference soils at the beginning of the experiment, resulted in high C storage. The highest values of SOC pool after application of sewage sludge, compost and lacustrine chalk to the soil from the zinc smelter area were obtained (Fig. 3(A)). Sewage sludge and compost were characterized by a high amount of HA and SOM content. Thus, these soil additives could have a tendency to humification of organic matter in the soil. A similar phenomenon, after the application of organic-inorganic fertilizers, was also noted by Brar et al. [38] and Fortuna et al. [62]. In turn, the highest values of soil organic carbon pool for the soil collected from coal mine was also recorded after the application of municipal compost. In addition, a higher value of soil organic pool in pots with pine was noted (Fig. 3(A)). As also confirmed by other studies, forest farming promotes carbon storage [63–65].

Similar results as for the soil organic carbon pool were also obtained for carbon stock in both soils. The reason for this could be recommended doses of fertilizer additives and short duration of the experiment. The highest of carbon stock values were observed after application of coal slurry and lacustrine chalk to smelter zinc soil, and after municipal compost application to brown coal mine soil (Fig. 3(B)). Especially high value of carbon stock, after the addition of coal slurry, can be explained by the low leaching and low mineralization

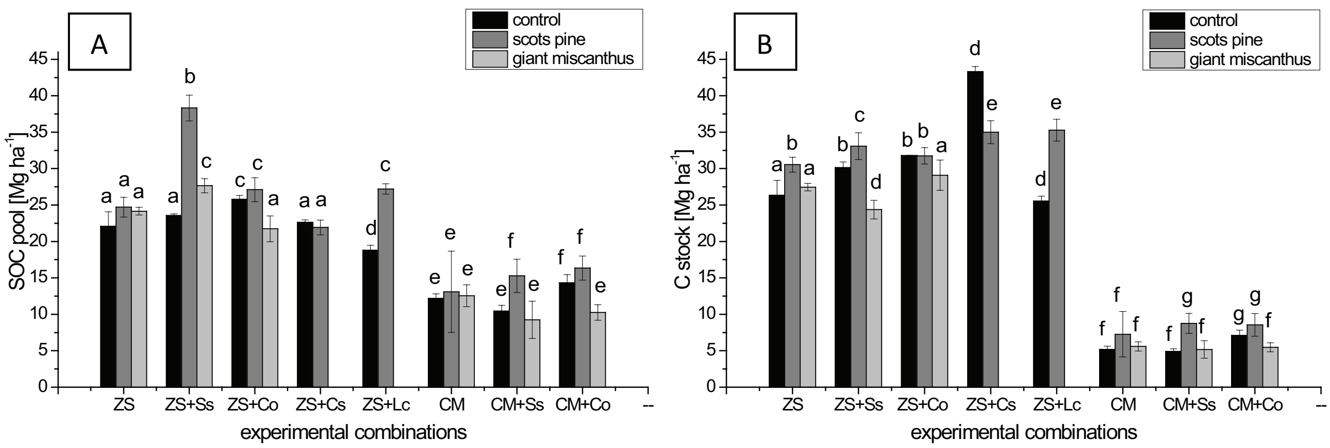

Fig. 3. Changes of soil organic carbon pool (A) and carbon stock (B) in two degraded soils. The letter combinations on X axis stand for ZS – zinc smelter soil, CM – brown coal mine soil, Ss – sewage sludge, Co – municipal compost, Cs – coal slurry, Lc – lacustrine chalk. Values are means with standard errors shown by the vertical bars (n = 2–3). Bars with the same letter(s) are not significantly different at $p \leq 0.05$.

of this soil amendment due to its origin. A similar trend of increased carbon stock after the application of organic-mineral soil additives was observed by other researchers [42,66]. In the cited studies, the highest of C stock values after the application of organic fertilizer (i.e., organic manure) in combination with NPK fertilizers was observed. Thus, in this case the combination effects of organic and mineral fertilization were the most effective. Moreover, in most cases, the highest values of this parameter were recorded in pots with pine. As already noted, forest management is conducive to the accumulation of soil organic matter and carbon sequestration, while preventing the escape of carbon from soils [67,68]. These methods are used primarily to determine the degree of soil organic carbon accumulation after long-term field experiment or in natural ecosystems, such as forest, when the initial carbon concentration in soils is unknown.

3.4. Changes in carbon sequestration rate and soil organic carbon build up rate in soils

Carbon storage and sequestration was also estimated on the basis of two further indicators, that is, carbon sequestration rate (Fig. 4(A)) and soil organic carbon build up rate (Fig. 4(B)). Their values were affected by the application of fertilizer additives and two plant species in both soils. These methods include a comparison between the initial and the final soil organic carbon concentration, and also between soil organic carbon content in treatment soil and reference soil [42,69]. As previous methods, carbon sequestration rate and soil organic carbon build up rate, take into account also soil depth and bulk density.

Similarly to carbon stock, high values of carbon sequestration rate after application of coal sludge and lake lacustrine chalk were obtained (Fig. 4(A)). Addition of these amendments contributed also to the increased soil organic carbon build up rate (Fig. 4(B)). All the organic-mineral soil additives contributed to carbon input (Figs. 1(C) and (D)). A similar effect of increased carbon sequestration rate after the application of soil amendments was observed in other studies [42]. In the cited study, the highest of C sequestration rate values after the application of mineral fertilizers and organic manure into two soils were noted in long-term fertilization experiment. As in the case of stock C values, the combination of organic fertilizer (i.e., organic manure) and NPK fertilizers were the most effective. Similar carbon sequestration efficiency in both soils was observed in our experiment, but carbon sequestration rate in pots with pine was higher than with miscanthus. Through the impact of the pine tree roots, less carbon leaching and increase in the organic matter storage was noted. The reason for this phenomenon could be less demand for soil nutrients by pine trees, in the initial stage of growth, than miscanthus.

Similar values of soil organic carbon sequestration rate and of soil organic carbon build up rate were reported (Figs. 4(A) and (B)). As stated earlier, the application of organic-mineral additives contributed to significant increase of TN, TC and TOC content and organic matter build up, and carbon sequestration in soils. The similar effect of soil fertilization was also obtained in other studies [69,70]. The cited studies have shown a much higher SOC sequestration rate and SOC build up rate after application of farmyard manure to the degraded soils. It was also important selecting the appropriate plant species. At the same time, the negative values of soil organic carbon build up rate were also noted. As in the case of carbon sequestration rate, increased soil organic carbon rate in pots with pine trees were estimated (Fig. 4(B)). In addition, significantly higher values of this characteristic of soil collected from brown coal mine were reported. This soil may manifest tendency to carbon storage, due to the high clay fraction.

These methods of estimation of carbon sequestration can be used in a short-term study and in the pot experiment (pot-grown plants). It is impossible to use SOC sequestration rate and SOC build up rate to calculate the SOC storage in natural ecosystem soils, when the initial carbon concentration is unknown.

3.5. Comparison of used methods calculating soil carbon sequestration

The comparison on the basis of soil organic carbon concentration and carbon sequestration indexes was made (Figs. 5–7). Therefore, the correlation of SOC pool and SOC

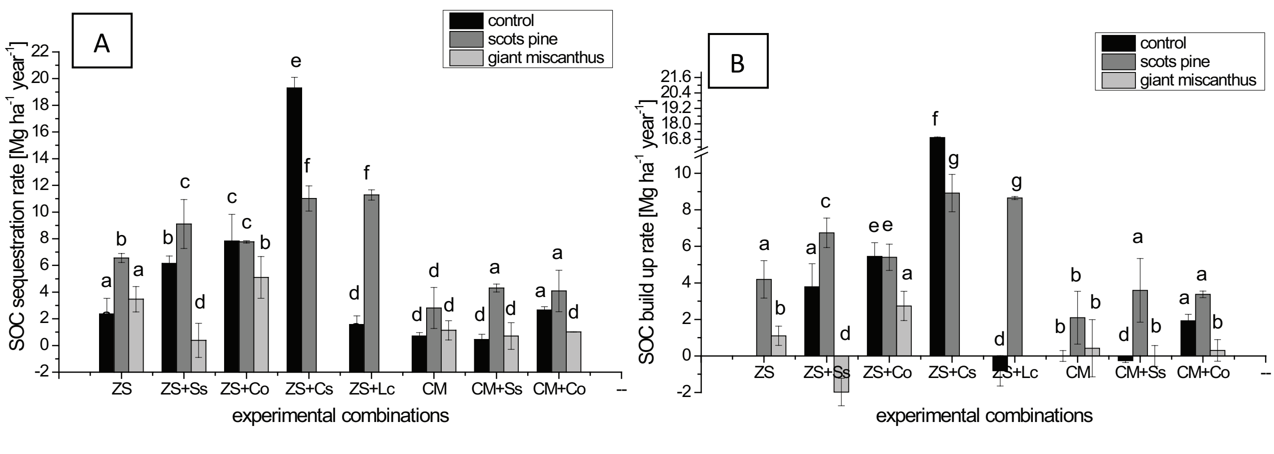

Fig. 4. Changes of carbon sequestration rate (A) and soil organic carbon build up rate (B) in two degraded soils. The letter combinations on X axis stand for ZS – zinc smelter soil, CM – brown coal mine soil, Ss – sewage sludge, Co – municipal compost, Cs – coal slurry, Lc – lacustrine chalk. Values are means with standard errors shown by the vertical bars (n = 2–3). Bars with the same letter(s) are not significantly different at $p \leq 0.05$.

stock, SOC build up rate and CMI, SOC build up rate and C sequestration rate was calculated.

The positive correlation of soil organic carbon pool and stock, for virtually all soil treatments, was noted (Fig. 5). Properly the same soil properties (carbon concentration, soil depth and bulk density) were used in the calculation of these indexes, hence a strong and consistent correlation was found. The strength and direction of a linear relationship between SOC pool and SOC stock was strongly dependent on the amount of soil organic carbon. The soil organic carbon pool and the carbon stock are similar methods and often used in the field experiments for measuring soil organic carbon sequestration [38–42].

Another correlation was calculated for the SOC build up rate and CMI (Fig. 6). These methods have been selected due to similar consideration of soil organic carbon content in treatment soil and reference soil. Therefore, in these methods the emphasis on the type of used soil amendments was put. The low correlation between SOC build up rate and CMI was indicated considering the fact, that the CMI includes different carbon forms in soil, including labile soil carbon. Studying the influence of plants, a weak, positive correlation between SOC build up rate and CMI was found. CMI is a method often used in calculating soil carbon sequestration, because of the multitude of factors taken into consideration [41,60].

The last correlation between SOC build up rate and C sequestration rate was calculated (Fig. 7). Both methods include a comparison between the initial and the final soil organic carbon concentration, and also between soil organic carbon content in treatment soil and reference soil. Studying the interaction of plants, the strong, positive linear relationship between SOC build up rate and C sequestration rate was noted. Both methods are often used in short- and long-term study and also in pot and field experiments [42].

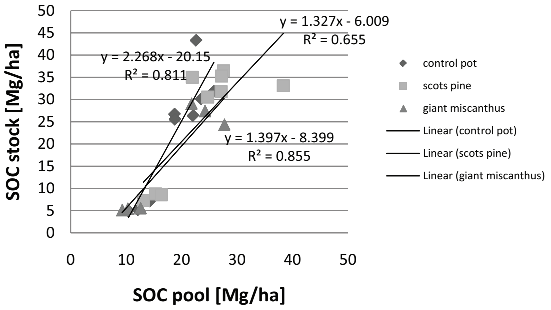

Fig. 5. Correlation between SOC stock and SOC pool in degraded soil of zinc smelter and post-mining areas.

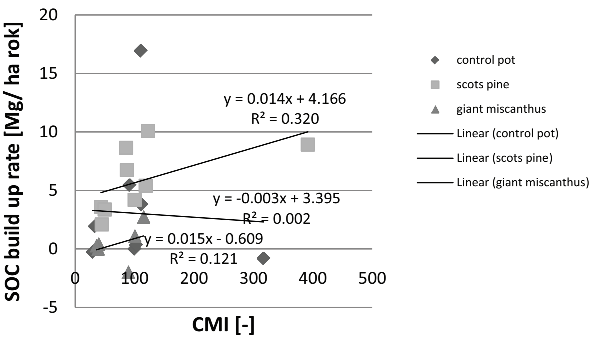

Fig. 6. Correlation between SOC build up rate and CMI in degraded soil of zinc smelter and post-mining areas.

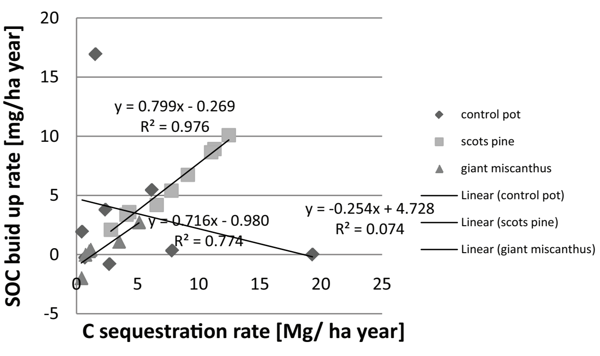

Fig. 7. Correlation between SOC build up rate and C sequestration rate in degraded soil of zinc smelter and post-mining areas.

4. Conclusion

Soil carbon sequestration is difficult to estimate, especially during short-term pot experiment. To draw conclusions from the experiment, a series of indexes there were used. The positive correlation of soil organic carbon pool and stock, for virtually all soil treatments, was noted. These methods are used primarily to determining the degree of soil organic carbon accumulation after long-term field experiment or in natural ecosystems, such as forest. In turn, the low correlation between SOC build up rate and CMI was indicated considering the fact, that the CMI includes different carbon forms in soil, including labile soil carbon. Studying the influence of plants, a weak, positive correlation between SOC build up rate and CMI was found. CMI is a method often used in calculating soil carbon sequestration, because of the multitude of factors taken into consideration. Moreover, studying also the interaction of plants, the strong, positive linear relationship between SOC build up rate and C sequestration rate was noted. Both methods are often used in short- and long-term study and also in pot and field experiments. The estimation of the efficiency of carbon sequestration in the pot experiment makes sense, if we treat this experiment as a short test. In our case, the aim of this test was to determine the most efficient soil amendments and suitability of plants in improving the soil health and quality during the phytoremediation process. At the same time, the aim of this test was also the soil carbon sink and storage. As the most useful fertilizer additives were considered lacustrine chalk and coal sludge. In turn, the most suitable plant that could be used in phytoremediation of degraded soils focused on carbon storage was a pine tree. The CMI and SOC sequestration rate were the best methods to determine carbon sequestration in the soil during conducted pot experiment.

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