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The effect of biochar on migration of selected heavy metals to soil, waters and plant biomass and physical and chemical properties of soil

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ABSTRACT

In general, biochar used to improve soils has a positive effect on their physical, chemical, and microbiological properties. Most often, it improves yielding and processing quality of biomass. However, due to the risk of introducing a number of xenobiotics into the soil with biochar, such as heavy metals, polycyclic aromatic hydrocarbons, or phenols, the quality and properties of this product should be monitored on regular basis. The main aim of the study was to analyze the effect of the use of biochar to enrich soils on their sorption properties. Three types of sandy soils were used for biochar fertilization. Biochar from burning of *Sida hermaphrodita* was added to the soils with the amounts of 1% and 2%. pH (active acidity), hydrolytic acidity (potential acidity), nitrogen and phosphorus content, organic matter, total carbon, and heavy metals were studied. Migration of heavy metals to soil waters and *S. hermaphrodita* biomass from soils fertilized with biochar were also studied. The use of 1% and 2% biochar for fertilization of sandy soils did not significantly reduce the mobility of heavy metals in soils and the accumulation of these elements in the examined plants. The content of heavy metals in the infiltrating water from most of the research objects ranged from Class 2 (good quality water) to Class 3 (satisfactory quality water) for groundwater.

Keywords: Biochar; *Sida hermaphrodita*; Fertilization; Soil; Soil waters; Heavy metals

1. Introduction

Biochar is most often used to improve the physical and chemical properties of soils. Its use as a fertilizer has an effect on plant yielding. With its valuable properties such as high organic carbon content, high chemical stability, extensive specific surface area, and porosity, biochar can also be used for soil carbon sequestration and optimization of the composting process. Based on biochar, fertilizers may be produced for the remediation of soils contaminated with organic and inorganic substances, improvement of soil properties, stimulation of plant growth, reduction of groundwater and surface water pollution, and removal of contaminants [1,2].

This material is not regarded in Poland as a typical fertilizer. Biochar may, however, be exceptionally considered an organic fertilizer or soil conditioner. The procedure for the approval of the use of biochar in Poland as a fertilizer or soil conditioner is the same as in the case of fertilizers and conditioners. It requires marketing authorization in accordance with the applicable legal acts, that is, the Act of 10 July 2007 on fertilizers and fertilization [3] and the Ordinance of the Minister of Agriculture and Rural Development of 18 June 2008 on the implementation of certain provisions of the Act on fertilizers and fertilization [4]. The act imposes the following limits on these fertilizer materials: Cr(100 mg), Cd(5 mg), Ni(60 mg), Pb(140 mg), and Hg(2 mg) per kg of dry matter of the tested fertilizer or soil conditioner.

The Ordinance does not take into account pollutants such as polycyclic aromatic hydrocarbons (PAHs), furans, dioxins, or polychlorinated biphenyls, with their quantity standardized in, for example, the US recommendations.

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Biochar can also have a significant effect on the reaction of the soil and soil waters. Some authors [5,6] emphasized that the higher the temperature of biomass combustion during the formation of biochar, the greater the deacidification effect after introduction into the soil.

Due to the risk of introducing a number of xenobiotics contained in biochar into the soil, including heavy metals, PAHs and phenols, the quality and properties of this product should be constantly monitored. Harmful compounds which may be present in biochar (incorrectly prepared or obtained from contaminated biomass) may migrate from the fertilized soil to groundwater and adversely affect plants and animals fed with such biomass. Changes in the pH of soils fertilized with biochar may also be subject to significant fluctuations, which may contribute to the uncontrolled migration of various contaminants [5].

The authors of the present research attempted to evaluate physical and chemical properties of biochar and its suitability as a soil conditioner. The aim of the study was also to evaluate the effect of the application of the biochar used for fertilization on possible migration of selected contaminants (heavy metals) to soil waters and plant biomass.

2. Material and methods

2.1. Examinations of biochar and soils used in the experiment

Tested samples of biochar formed after pyrolysis of *Sida hermaphrodita* at 450°C (Fig. 1) were initially dried at room temperature, crushed, and passed through a sieve with 2 mm mesh. Next, they were dried at 105°C to constant weight, ground in a mortar and sieved again through a sieve with a mesh diameter of 0.6 mm.

The soil was also dried to constant weight in the air and passed through a sieve with a mesh diameter of 1 mm. The following determinations were made [7]:

- pH in water: the potentiometric method,
- pH in KCl: the potentiometric method,
- total carbon (TC): determined by means of a Multi N/C 2100, Analytik Jena AG, Jena (Germany) carbon analyzer,
- Kjeldahl nitrogen: determined by distillation after prior mineralization of samples in a Buchi K-435, Buchi Labortechnik AG Company, New Castle (The United States of America) mineralizer,
- content of organic matter: the weighing method,
- content of available forms of phosphorus: the Egner-Riehm method,
- total phosphorus: determined by means of the spectrophotometric method with ammonium molybdate (samples were previously mineralized in a Berghof high-pressure microwave mineralizer).

The total contents of heavy metals, that is, mercury (Hg), copper (Cu), lead (Pb), cadmium (Cd), zinc (Zn), nickel (Ni), chromium (Cr), arsenic (As), and molybdenum (Mo) in biochar and sandy soils were also evaluated. Aqua regia (a mixture of concentrated hydrochloric and nitric acids at a volumetric ratio of 3:1) was used for the extraction of metals. Mineralization was conducted at 180°C for 30 min, using a high-pressure microwave mineralizer MWS-2, BERGHOF, Products and Instruments GmbH, Eningen (Germany).

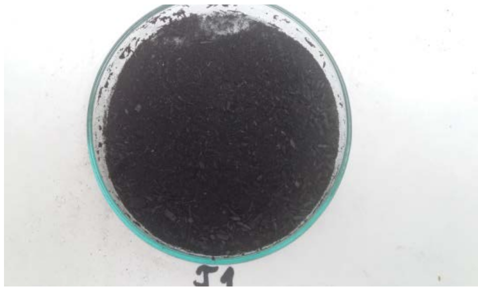

Fig. 1. Biochar from *Sida hermaphrodita* after pyrolysis at 450°C (after crushing).

The contents of heavy metals were evaluated by means of an inductively coupled plasma optical emission spectrometers SPECTRO ARCOS FHX22, SPECTRO Analytical Instruments GmbH, Kleve (Germany).

The content of total organic carbon (TOC) in biochar water extract was determined using a Multi N/C 3100 Analytik Jena carbon analyzer.

The content of mercury (Hg) was determined directly in the sample by means of the AMA254 mercury analyzer—atomic absorption spectrometer.

Polish guidelines do not provide for requirements for the determination of PAHs in biochar. However, PAHs were also determined due to the presence of tarry compounds (which can be dangerous, e.g., plants and soil organisms) in water extracts of the tested biochar.

The initial stage before chromatographic determination of PAHs in biochar was extraction with organic solvents of different polarity. The separation of the organic matrix was carried out using sonolysis using a mixture of cyclohexane and dichloromethane solvents (5:1 v/v). Separation of solvent extracts from the sample was carried out with a high-speed centrifuge. Silica gel was used to isolate the analyzed components from the extracts from other simultaneously extracted organic substances, with purification conducted under vacuum conditions. The treated extracts were concentrated in the nitrogen stream. The determination was performed using a gas chromatograph coupled to a mass spectrometer (Fisons GC800/MS800, New Jersey, The United States of America). The study determined 16 PAHs indicated on the EPA list for environmental analyses [8]. These were: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo(a)pyrene, dibenz [a,h] anthracene, benzo[ghi]perylene, and indeno[1,2,3-cd]pyrene.

Three types of sandy soil were used for fertilization with biochar (loamy sand), derived from selected areas of large *S. hermaphrodita* plantation. The soils were marked according to the location of sampling (D, S, BS). Biochar was introduced into the examined soils with the amounts of 1% and 2%. The control substrate was non-fertilized soil (marked as C in each of the three soils).

Virginia fanpetals (*S. hermaphrodita*) were cultivated on the prepared soil mixtures. The study was conducted under conditions of pot experiment in a foil tunnel. The pots used for the study had a capacity of 12 L. They were adapted to the sampling of soil water leachates. Root seedlings from the *S. hermaphrodita* plantation areas were used for planting. During the experiment, the constant moisture content in the substrates (60%) was maintained in the pots (evaluated by weight method). The example research objects are presented in Fig. 2.

2.2. Examinations of soil, leachates, and plant biomass at the end of the experiment

The following parameters were analyzed in the fertilized soils after completion of the experiment: reaction of soil mixtures (active acidity), hydrolytic acidity (potential acidity), saturation of the sorption complex with alkalis, available nitrogen and phosphorus content, and contents of organic matter, total carbon, and heavy metals (as during examination of biochar and control soil), according to the recommended methodology [7,9].

Heavy metals were determined in water leachates from fertilized soils and biomass *S. hermaphrodita* according to the methodology described above.

Vegetation tests were conducted for a period of 6 months (from May to October 2018), with three repetitions. The results are represented by the means from these repetitions.

Analysis of the results was performed by means of a statistical software package STATISTICA 9.0. The significance of statistical differences was examined compared to control samples. The test probability of $p < 0.05$ was assumed to be significant and the test probability of $p < 0.01$ was considered highly significant.

3. Results

Results of chemical tests (heavy metals) for biochar obtained from *S. hermaphrodita* and their comparison with the Polish fertilizing recommendations [3.4], which set out the maximum permissible amount of contaminants in fertilizers and soil conditioners, are presented in Table 1. Other physical and chemical properties of the biochar studied are presented in Table 2.

Table 3 also presents a comparison of the results of biochar obtained from *S. hermaphrodita* with other binding standards for this type of products in some European countries (European Biochar Foundation, EBF) and (International Biochar Initiative, IBI) in the United States [10]. The content of polycyclic aromatic hydrocarbons not included in Polish standards was also taken into account.

Fig. 2. Examples of research objects with *Sida hermaphrodita* cultivated on soil mixtures (BS): from the left: control soil, with 1% and 2% of biochar doses.

Physical and chemical characterization of the soils used in the experiment (before fertilization) is presented in Table 4.

The results of the examinations of selected physicochemical parameters affecting fertility and sorption properties of soils in soil mixtures from individual research objects after completion of the experiment are presented in Table 5.

Contents of heavy metals in soil mixtures from individual research objects fertilized with biochar after completion of the experiment are presented in Table 6.

Contents of heavy metals in biomass of *S. hermaphrodita* from individual research objects fertilized with biochar after completion of the experiment are presented in Table 7.

Table 2
Physical and chemical characterization of biochar used in the pot experiment

Parameter	Biochar
pH (in H_2O)	4.60
pH (in KCl)	4.35
Total carbon (TC) [%]	63.2
Nitrogen content (N) [%]	0.7
Phosphorus content (P) [%]	0.2
Potassium content (K) [%]	0.4
TOC (in water extract) [mg/L]	3,580
Calcium content (Ca) [%]	1.2

Table 1
Results of chemical determinations (heavy metals) in the biochar studied obtained from *Sida hermaphrodita* and the contents of these elements in fertilizers permissible in Poland

Heavy metal	Content of contaminants determined in biochar (mg/kg d.m.)	Maximum permissible content of contaminants in fertilizers (mg/kg d.m.) [4]
Chromium (Cr)	28.0	100
Cadmium (Cd)	<2.0	5
Nickel (Ni)	2.5	60
Lead (Pb)	5.1	140
Mercury (Hg)	0.010	2

d.m., dry matter.

Table 3
Comparison of the results of chemical analyses of the tested biochar from the *Sida hermaphrodita* with the guidelines for biochar in selected European countries and the USA

Type of contaminant present in biochar (mg/kg d.m.)	Content of contaminants determined in biochar	Permissible values according to the European Biochar Certificate (EBC)	Permissible values according to the International Biochar Initiative (IBI)
Arsenic (As)	<2.0	13	13–100
Cadmium (Cd)	<2.0	15	1.4–39
Chromium (Cr)	28	90	93–1,200
Copper (Cu)	16.0	1,000	143–6,000
Mercury (Hg)	0.010	1	1–17
Nickel (Ni)	2.5	50	47–420
Lead (Pb)	5.1	150	121–300
Zinc (Zn)	46.0	400	416–7,400
Selenium (Se)	n.m.	–	2–200
Molybdenum (Mo)	4.4	–	5–75
Fluorine (F)	2,730	–	–
PAHs (16)	1,413	12	6–300
PCB	n.m.	0.2	0.2–1
Dioxins and furans [ng/kg d.m.]	n.m.	20	20

n.m., not marked; d.m., dry mass.

Table 4
Physical and chemical characterization of soils used in the pot experiment

Parameter	Soil		
	D	S	BS
pH (in H_2O)	6.43	6.72	7.12
pH (in KCl)	5.88	6.42	6.66
Hydrolytic acidity (H_h) [me/100 g]	0.92	0.90	0.71
P_2O_5 [mg/100 g soil]	5.1	8.7	5.6
Kjeldahl N [mg/kg]	1,197	1,376	949
Total carbon (TC) [mg/g]	16.5	13.0	18.5
Organic matter content (loss on ignition) [%]	1.95	1.61	2.56
Lead (Pb) [mg/kg d.m.]	19.6	16.3	22.9
Zinc (Zn) [mg/kg d.m.]	37.7	29.4	38.4
Copper (Cu) [mg/kg d.m.]	4.3	3.0	6.8
Nickel (Ni) [mg/kg d.m.]	10.3	3.9	16
Cadmium (Cd) [mg/kg d.m.]	<0.44	<0.44	<0.44
Chromium (Cr) [mg/kg d.m.]	20.3	0.6	26.0
Mercury (Hg) [mg/kg d.m.]	n.d.	n.d.	n.d.

n.d., not detected

Contents of heavy metals in infiltrating water from individual research objects fertilized with biochar after completion of the experiment are presented in Table 8.

4. Discussion

Currently, there is no standardized definition of biochar and no separate regulations concerning the production and use of this material both in Poland and in other European countries. Discrepancies in the nomenclature and classification of biochar are substantial. Depending on the properties and suitability for use, biochar can be considered an organic fertilizer or soil conditioner. Drying, pyrolysis, and gasification of the introduced biomass take place during a process termed torrefaction. The results include a loss of about 30% of mass, formation of the so-called torgas, and obtaining biochar. The product is similar to charcoal but there are some differences. The definition of biochar is also provided in the recommendations of the European Biochar Certificate (ECB) [5]. According to them, biochar is a heterogeneous material, rich in aromatic carbon and minerals, which is produced as a result of biomass pyrolysis. The recommendations also

Table 5
Characteristics of selected physicochemical parameters in soils fertilized with biochar

Determination	Soil								
	1			2			3		
	D C	D +1%	D +2%	S C	S +1%	S +2%	BS C	BS +1%	BS +2%
pH (in H_2O)	6.99	7.29*	7.53**	7.67	7.82*	8.09**	7.55	7.60s.i.	7.70*
pH (in KCl)	6.51	6.67*	6.87**	7.01	7.42*	7.63**	6.91	6.99s.i.	7.11*
Hydrolytic acidity (H_h) [me/100 g]	0.98	0.90*	0.90*	0.90	0.60**	0.53**	0.75	0.65**	0.60**
P_2O_5 [mg/100 g soil]	6.5	6.7s.i.	6.9s.i.	8.2	15.8**	16.3**	3.8	4.3*	6.0**
Kjeldahl N [mg/kg]	1,008	1,114*	1,211*	938	1,183**	1,173**	1,232	1,243s.i.	1,344**
TC [mg/g]	17.13	21.62**	30.02**	13.06	23.71**	24.69**	20.09	24.43**	24.74**
Organic matter content (loss on ignition) [%]	2.06	2.53*	3.75**	1.78	2.90**	2.93**	2.82	3.48**	3.60**

Significance of differences: *p < 0.05, **p < 0.01; s.i., statistically insignificant difference.

Table 6
Contents of heavy metals in soils from individual research objects fertilized with biochar after completion of the experiment

Heavy metal (mg/kg d.m.)	Soil								
	1			2			3		
	D C	D +1%	D +2%	S C	S +1%	S +2%	BS C	BS +1%	BS +2%
Lead (Pb)	18.0	18.5s.i.	18.8s.i.	16.4	16.5s.i.	16.6s.i.	22.8	22.6s.i.	23.5s.i.
Zinc (Zn)	39.8	38.4s.i.	37.8s.i.	32.9	40.0*	40.1*	43.1	41.8*	40.1*
Copper (Cu)	7.5	7.4s.i.	6.8s.i.	6.4	6.9s.i.	7.9*	17.3	12.0**	9.6**
Nickel (Ni)	8.5	7.8s.i.	6.1*	7.4	6.9s.i.	6.5s.i.	13.5	14.5s.i.	22.1**
Cadmium (Cd)	0.8	<0.44	<0.44	<0.44	<0.44	0.7	<0.44	<0.44	<0.44
Chromium (Cr)	10.7	9.97s.i.	10.9s.i.	9.4	9.5s.i.	8.9s.i.	22.7	21.9s.i.	22.1s.i.
Mercury (Hg)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d., not detected; d.m., dry mass.
Significance of differences: *p < 0.05, **p < 0.01; s.i., statistically insignificant difference.

Table 7
Contents of heavy metals in plant biomass from individual research objects fertilized with biochar after completion of the experiment

Heavy metal [mg/kg d.m.]	Biomass								
	1			2			3		
	D C	D +1%	D +2%	S C	S +1%	S +2%	BS C	BS +1%	BS +2%
Lead (Pb)	<4.28	<4.28	<4.28	<4.28	<4.28	<4.28.	<4.28	<4.28	<4.28
Zinc (Zn)	13.1	13.0s.i.	12.1s.i.	15.54	17.76*	22.6**	23.4	44.2**	46.9**
Copper (Cu)	2.7	2.6s.i.	2.57s.i.	2.63	2.53s.i.	6.19**	3.9	8.91**	9.0**
Nickel (Ni)	<0.87	<0.87	0.95	<0.87	<0.87	1.23**	0.95	5.4**	5.6**
Cadmium (Cd)	0.7	0.5*	0.5*	0.5	0.6s.i.	0.6s.i.	0.5	0.6s.i.	0.6s.i.
Chromium (Cr)	n.d.	n.d.	0.30	n.d.	0.50	0.56	n.d.	n.d.	n.d.
Mercury (Hg)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d., not detected; d.m., dry mass.
Significance of differences: *p < 0.05, **p < 0.01; s.i., statistically insignificant difference.

define the range of temperatures in which the thermal process is carried out (from 350°C to 1,000°C) and at the same time excludes the material resulting from torrefaction or hydrothermal carbonization. A criterion of carbon content was also adopted in the ECB. Biochar is a material that contains more than 50% carbon in dry matter. A material that contains less than 50% carbon is referred to as a pyrogenic carbon material.

Table 8
Contents of heavy metals in infiltrating water from individual research objects fertilized with biochar after completion of the experiment

Heavy metal [mg/L]	Water								
	1			2			3		
	D C	D +1%	D +2%	S C	S +1%	S +2%	BS C	BS +1%	BS +2%
Lead (Pb)	0.1	0.1s.i.	n.d.	0.1	0.1s.i.	n.d.	n.d.	n.d.	n.d.
Zinc (Zn)	0.8	1.1*	1.3**	1.1	1.2s.i.	1.2s.i.	1.4	1.8*	1.8*
Copper (Cu)	0.03	0.04s.i.	0.04s.i.	0.05	0.08*	0.09*	0.06	0.10*	0.12*
Nickel (Ni)	0.01	0.01s.i.	0.02*	0.01	0.01s.i.	0.01s.i.	0.01	0.02*	0.02*
Cadmium (Cd)	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005
Chromium (Cr)	n.d.	n.d.	0.02	n.d.	0.04	0.04	n.d.	n.d.	n.d.
Mercury (Hg)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d., not detected.
Significance of differences: *$p < 0.05$, **$p < 0.01$; s.i., statistically insignificant difference.

The analysis of the content of heavy metals in the examined biochar and comparison with the standards permissible in Poland indicates the lack of contamination with these elements and their usefulness for soil fertilization (Table 1). The results indicate that the material tested can be characterized as biochar because the content of total carbon exceeds 50% (63.2%). The content of calcium (1.2%) is important in this material. However, the very low reaction of 4.6 (in H_2O) is alarming. During the examinations, a brown coloring of water extracts obtained from biochar was also observed, which may indicate the presence of tarry compounds. This is also evidenced by the high content of organic carbon (TOC) in the biochar tested, amounting to 3,580 mg/L. It is likely that during the torrefaction process, the biomass was not fully burnt. These conditions may lead to an increased content of PAHs. However, this was not confirmed by the study results.

The tests of the presence of polycyclic aromatic hydrocarbons in biochar did not show an increased concentration of these compounds (Table 3). The total content of 16 PAHs in the tested biochar was 1.413 mg/kg d.m. Table 2 also presents a comparison of the results of the examinations of biochar obtained from *S. hermaphrodita* with other binding standards for this type of product in some European countries (EBF) and (IBI) in the United States [10]. Also in this case, the results of biochar tests do not exceed the permissible limits.

A significant factor that determines such effects as mobility of heavy metals and other chemical pollutants in soil is sorption properties of the soil. The soils studied (Table 4) were characterized by a high pH. Soil marked as D (with pH 6.43) can be classified as neutral, soil S (pH 6.72) is weakly alkaline, and BS (pH 7.12) is medium-alkaline [7]. This is also confirmed by the determination of hydrolytic acidity in the soils, amounting to 0.92, 0.90, and 0.71 me/100 g, respectively. In Poland, on average, in light arable soils (with a small capacity of a sorption complex), H_h values usually vary from 1 to 3 me per 100 g of soil [11].

Analysis of the results of physical and chemical properties of soils after biochar fertilization (Table 5) revealed that its application to all soils caused an increase in pH (active acidity), a decline in hydrolytic acidity (potential acidity), an increase in sorption capacity, and an increase in the contents of phosphorus, nitrogen, total carbon, and organic matter. Similar results were obtained by Nigussie et al. [12]. The authors found that the biochar added to poor and degraded soils may contribute to the improvement of soil fertility and productivity.

An increase in the reaction of the fertilized soils was observed in the study in all the fertilized soils after the use of biochar. Similar results of biochar effect on soil acidity were found by previous authors [13]. A long-term effect of fertilization on soil reaction and tendencies which might be unnoticed during the determination of active acidity can be more measurably determined by potential acidity (so-called hydrolytic acidity). After fertilization with biochar, acidity also decreased with increasing doses. Biochar had an alkalizing effect on the soil environment in all cases. This was interesting from the scientific point of view, since examinations of biochar (Table 2) revealed an alarmingly low pH 4.6 (in H_2O), which may suggest the insufficient temperature of combustion of *S. hermaphrodita* biomass [6]. However, our results did not confirm these findings. The increase in pH of the fertilized soils was probably caused by the high calcium content (1.2%) in the biochar studied (Table 2). It was gradually released in the soil environment, increasing its pH.

Fertilization with biochar also increased sorption capacity. This is likely to be caused by an increase in the total amount of carbon and organic matter in fertilized soils. Total carbon (TC) after soil fertilization with biochar with doses of 1% and 2% increased compared to control samples by 26.2% and 75.2% for soil D, 81.6% and 89.1% for soil S, and 21.6% and 23.1% for soil BS. The amount of organic matter in the soils also increased with the dose of the biochar applied. Similar positive effects of the use of biochar in soil amendment in a vineyard were documented by Prodana et al. [13]. These researchers found improvements in the physical and chemical properties of soils, including sorption complex. However, 18 months after fertilization, they observed a negative effect of biochar application on selected soil microorganisms, which could be linked to biochar properties or to its interaction with conventional crop protection agents. The authors recommend biochar quality control before its application as a fertilizer. The researchers found that the addition of biochar for fertilization purposes does not prevent the long term accumulation of contaminants in plants. Similar results were found in the case of sandy-clay soils after the application of 50 t/ha of biochar obtained from maize by Andrés et al. [14]. In their study, the addition of biochar significantly reduced the biomass of soil microorganisms. However, it did not change the functional microbiological diversity, abundance, and biodiversity.

The cation exchange capacity (number of cations with the alkaline character) rose with the dose of the introduced biochar. Similar results concerning the positive effect of the biochar used on soil sorption properties were observed for light soils by El-Naggar et al. [15].

The analysis of the determined contents of heavy metals in soils fertilized with biochar (Table 6) showed that the values for agricultural soils permissible in Poland were not exceeded. The permissible amounts of heavy metals in such soils are (in mg/kg d.m.): 150 for chromium, 300 for zinc, 2 for cadmium, 100 for copper, 100 for nickel, 100 for lead, and 2 for mercury [9]. Another comparison [11] shows a zero level of heavy metal contamination of the soils studied. They may be used in agriculture for any purposes.

The study did not find that the biochar added to the soil significantly reduced the bioaccumulation of heavy metals in plants, which was demonstrated by Nigussie et al. [12]. The content of heavy metals determined in the biomass of *S. hermaphrodita* (Table 7) indicates that fertilization with biochar did not cause a significant increase in the bioaccumulation of these elements. A statistically significant increase was found only in the content of copper and nickel in plants from soil BS and in the content of zinc in soils S and BS after application of 1% and 2% of biochar. However, the bioaccumulation of all heavy metals was within the range of the contents observed in plants in the natural environment [11].

An important element of the research was to determine whether the addition of biochar to the soil reduces the amount of leached components, including heavy metals. It is often emphasized in the literature that water retention in soil improves after biochar application due to the porous structure of this material [5]. However, some authors [16] failed to find such biochar properties in their studies. Wang et al. [16] used walnut biochar introduced into the soil in the amount of 0.5%–1%. However, they analyzed clay soil with low porosity. The authors emphasize that sandy soils can demonstrate a better response to fertilization with biochar. The researchers also found no increased accumulation of components in the biochar pores, which could inhibit the mobility of contaminants. A similar phenomenon was also observed in our study. Other results were documented by Karhu et al. [17] after the application of 5 t/ha biochar found an 11% increase in water capacity.

The study did not find whether soil fertilization with biochar significantly reduced the leaching of heavy metals from the soil. However, the results of heavy metal determination in infiltrating water from soils fertilized with biochar (Table 8) showed that there was no significant increase in contamination with these elements and no deterioration in the quality of the environment. This was probably due to the low contents of contaminations in the sandy soil and the biochar used. However, in soils contaminated with heavy metals, there may be a risk of soil water contamination despite the application of 1% and 2% biochar doses. In the analyzed experimental objects, the content of heavy metals in water from most soil mixtures was within the range of Class 2 (good quality water) and Class 3 (satisfactory quality water) of groundwater [18].

5. Conclusions

- The results of chemical composition tests of the analyzed biochar showed no contamination with heavy metals and other components and the opportunities for using it for fertilizing purposes.
- It was found that the content of heavy metals in soils fertilized with biochar did not exceed the levels permissible for agricultural use.
- The results obtained for physical and chemical properties of soils after fertilization with biochar showed that application of only this fertilizing material caused an increase in pH, sorption capacity, a decline in hydrolytic acidity (potential acidity), and increase in the content of phosphorus, nitrogen, total carbon, and organic matter.
- The use of 1% and 2% biochar for fertilization of sandy soils did not significantly reduce the mobility of heavy metals in soils and the accumulation of these elements in the examined plants.
- The bioaccumulation of all heavy metals in the biomass of *S. hermaphrodita* was within the range of the contents found in plants in the natural environment. Plant material can be used, for example, composting.
- The content of heavy metals in the infiltrating water from most of the research objects ranged from Class 2 (good quality water) to Class 3 (satisfactory quality water) for groundwater.

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References

[1] K. Malińska, Biochar is the answer to current problems environmental protection, Eng. Environ. Prot., 4 (2012) 387–403 (In Polish).

[2] A. Anstey, S. Vivekanandhan, A. Rodriguez-Uribe, M. Misra, A.K. Mohanty, Oxidative acid treatment and characterization of new biocarbon from sustainable *Miscanthus* biomass, Sci. Total Environ., 550 (2016) 241–247.

[3] Act of 10 July 2007 on Fertilizers and Fertilization, Dz. U. Nr 147, poz. 1033 (In Polish).

[4] Regulation of the Minister of Agriculture and Rural Development of 18 June 2008 on the Implementation of Certain Provisions of the Act on Fertilizers and Fertilization, Dz.U. z 2008 r. nr 119, 765 (In Polish).

[5] J. Gładki, Biochar as a chance for sustainable development, Printing House Apla Sp.J., Copyright© by Fluid S.A., Sędziszów, 2017 (In Polish).

[6] M.K. Hossain, V. Strezov, K.Y. Chan, A. Ziolkowski, P.F. Nelson, Influence of pyrolysis temperaturę on production and nutrient

properties of wastewater sludge biochar, J. Environ. Manage., 92 (2011) 223–228.

[7] A. Ostrowska, S. Gawlinski, Z. Szczubiałka, Methods of Analysis and Evaluation of Soil and Plant Properties, Catalog of the Institute of Environmental Protection, Warszawa, Poland, 1991 (In Polish).

[8] Polycyclic Aromatic Hydrocarbons (PAHs) Standards EPA. Available at: https://ec.europa.eu/jrc/sites/jrcsh/files/Factsheet%20PAH_0.pdf (downloaded 30. 08. 2019).

[9] Regulation of the Minister of the Environment of 1 September 2016 on the Method of Conducting the Assessment of Pollution of the Earth Surface. Available at: http://prawo.sejm.gov.pl/isap.nsf/download (In Polish) (downloaded 30. 08. 2019).

[10] K. Malińska, K. Mełgieś, Current quality and legal requirements for biofuel as a fertilizer and soil improver, Work ICiMB, 26 (2016) 82–95 (In Polish).

[11] A Kabata-Pendias, M. Piotrowska, T. Motowicka-Terelak, Fundamentals of Evaluation of Chemical Soil Contamination (Heavy Metals, Sulphur and PAH), State Inspectorate for Environmental Protection, IUNG in Puławy, Poland, 1995 (In Polish).

[12] A. Nigussie, E. Kissi, M. Misganaw, G. Ambaw, Effect of biochar application on soil properties and nutrient uptake of lettuces (*Lactuca sativa*) grown in chromium polluted soils, Am. Eurasian J. Agric. Environ. Sci., 12 (2012) 369–376.

[13] M. Prodana, A.C. Bastos, A. Amaro, D. Cardoso, R. Morgado, A.L. Machado, F.G.A. Verheijen, J.J. Keizer, S. Loureiro, Biomonitoring tools for biochar and biochar-compost amended soil underviticulture: looking at exposure and effects, Appl. Soil Ecol., 137 (2019) 120–128.

[14] P. Andrés, A. Rosell-Melé, F. Colomer-Ventura, K. Denef, M.F. Cotrufo, M. Riba, J.M. Alcañiz, Belowground biota responses to maize biochar addition to the soil of a Mediterranean vineyard, Sci. Total Environ., 660 (2019) 1522–1532.

[15] A. El-Naggar A., S.S. Lee, J. Rinklebe, M. Farooq, H. Song, A.K. Sarmah, A.R. Zimmerman, M. Ahmad, S.M. Shaheen, Y.S. Ok, Biochar application to low fertility soils: a review of current status, andfuture prospects, Geoderma, 337 (2019) 536–554.

[16] D. Wang, C. Li, S.J. Parikh, K.M. Scow, Impact of biochar on water retention of two agricultural soils – a multi-scale analysis, Geoderma, 340 (2019) 185–191.

[17] K. Karhu, T. Mattila, I. Bergstrom, K. Regina, Biochar addition to agricultural soil increased CH_4 uptake and water holding capacity - results from a short-term pilot field study, Agric. Ecosyst. Environ., 140 (2011) 309–313.

[18] Regulation of the Minister of the Environment of 21 December 2015 on Criteria and Methods for Assessing the Status of Bodies of Groundwater (In Polish).