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ORIGINAL PAPER

THE EFFECTIVENESS OF BIOCHAR IN MITIGATING CHANGES IN THE CHEMICAL PROPERTIES OF SANDY SOIL TREATED WITH VARIOUS CHEMICALS*

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Abstract

The progressive degradation of soils is a recently increasing environmental problem. The risk of soil degradation may be associated, for example, with landslides, flooding, soil erosion. However, these are relatively rare phenomena compared to the risk of chemical degradation caused by human activity. Given the limited research on the positive effect of miscanthus biochar on soil properties, a study was carried out aimed at determining changes in pH, electrical conductivity, sorption properties, and mobility of selected heavy metals in sandy soil treated with various chemicals. Biochar used in the study was produced at a temperature of 300°C. The addition of biochar to soil generally increased the pH value, regardless of the type of chemical degradation. The study revealed a decrease in the hydrolytic acidity value and, at the same time, no significant changes in the content of alkaline cations and sorption capacity of the biochar-treated soil. The best effect on reducing the mobility of trace elements was achieved by adding biochar to the soil supplemented with acidifying substances. Bearing in mind the current agricultural and environmental problems, there is a need to increase the effectiveness of biochar and to direct its action to improve specific soil properties.

Keywords: biochar, soil, sorption complex, pH, electrical conductivity, heavy metal.

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INTRODUCTION

Thermal transformation of waste biomass can be a promising approach to solve environmental problems. This process has a positive effect not only by disposing of substantial amounts of waste, but also by creating a product that can be widely applied, i.e. biochar. The interest in biochar expressed by scientists and practitioners has not been waning for several years and there are more and more potential applications of this product. Biochar enhances carbon sequestration and reduces greenhouse gas emissions. It is often used as a biofuel and a means for wastewater treatment, soil fertility enhancement, and reclamation of degraded soils (LEE et al. 2018). The properties of biochar largely depend on the pyrolysis temperature and on the type of feedstock. As reported by ZHAO et al. (2013), biomass transformed at ca. 200°C retains properties comparable to those of the feedstock used in the process. Only pyrolysis carried out at ca. 300°C changes the physical and chemical properties of the product, as well as the content of aliphatic and aromatic carbons in it (GAI et al. 2014). Wu et al. (2012) demonstrated that biochars produced at 300-400°C have the highest aromaticity. These authors also discovered that biochars produced at >400°C exhibit reduced functionality. lower hydrophilicity, and a reverse tendency towards oxidation. On the other hand, Wu et al. (2012) reported disintegration of functional groups induced by thermal degradation at temperatures above 600°C. Therefore, it can be concluded that efficiency of biochar depends on its production method.

The progressive degradation of soils is a recently increasing environmental problem, which leads to partial or complete loss of soil functions (ZHANG et al. 2016). The risk of soil degradation may result from landslides, flooding or soil erosion. However, these are relatively rare phenomena compared to the risk of chemical degradation caused by human activity (TOTH et al. 2008). Soil degradation depends largely on its properties and location. For example, if the soil is located near /8an industrial plant, it will be more exposed to degradation factors. In Poland, most soils are classified as light soils, and their quality is substantially deteriorated by acidification (FILIPEK and SKOWROŃSKA 2013). The problem of soil salinity and local alkalisation (not only in Poland) is increasingly being addressed (WIDŁAK 2016, SAIFULLAH et al. 2018). These degrading factors are a consequence of human industrial and agricultural activity. Changes in the chemical properties of soils significantly affect the biological activity in soil and the chemistry of soil processes, including changes in the trace element availability (BISWAS et al. 2018).

As shown in the available literature, the application of biochar to soil may cause decomposition of carbonates and hydroxides contained therein, thus increasing soil pH (KOOKANA et al. 2011, LUCCHINI et al. 2014). In turn, CHENG et al. (2006) argued that the application of biochar in soils can release acidifying substances through chemical and microbiological processes. This situation occurring in a short time (four months after the application) was

also confirmed by LIU and ZHANG (2012). Similarly, INAL et al. (2015) reported that the use of poultry litter biochar reduced the pH value in alkaline soil. LIU and ZHANG (2012) suggested that this may be associated with the release of acidic functional groups during biochar oxidation. As shown by ATKINSON et al. (2010), Ca and P may be bound in such conditions, consequently reducing the concentration of Ca ions in the soil solution.

Biochar application can greatly reduce the content of salts easily soluble in the soil solution (SOLAIMAN, ANAWAR 2015). This is related to the properties of biochar, primarily its sorption capacity (NARTEY, ZHAO 2014). GONDEK and MIERZWA-HERSZTEK (2016) proved that the feedstock used for biochar production has an important role in the inactivation of ions responsible for the increase/decrease of the soil solution electrical conductivity. These authors demonstrated that the application of pig manure and poultry litter biochars increased the soil electrical conductivity, proportionally to the biochar dose.

Scientific papers provide many divergent data on the biochar effect on soil properties (ZHANG et al. 2016). This situation is dictated not only by the conditions under which the experiment is carried out, but also by the parameters and the feedstock used to produce biochar. According to RASSE et al. (2017), durability is an important element in choosing the type of biochar. The cited authors demonstrated that miscanthus biochar is stable, and the estimated average time of its decomposition in soil is >100 years.

Given the limited volume of research on the positive effect of miscanthus biochar on soil properties, a study was carried out aimed at determining changes in pH, electrical conductivity, sorption properties, and mobility of selected heavy metals in sandy soil treated with various chemicals.

MATERIAL AND METHODS

The properties of the soil analysed in the study, sampled from the 0-0.2 m layer of an arable field in southern Poland, Malopolska province (50°09'34" N and 19°66'28" E), are shown in Table 1.

The process of thermal transformation of *Miscanthus giganteus* (miscanthus) straw was carried out under laboratory conditions in a facility for thermal transformation of biomass with limited access of air -1-2% (IBI 2012). The temperature in the combustion chamber was $300\pm10^{\circ}$ C. The combustion chamber heating rate was 10° C min⁻¹. Duration and temperature of pyrolysis were established in preliminary investigations and based on other authors' results (Lu et al. 2013). Some properties of miscanthus straw and biochar are shown in Table 2.

Miscanthus straw and biochar were 1 mm ground in a laboratory mill. Subsequently, dry matter content was determined after drying materials at 105°C for 12 hours. The control soil sample was air-dried and 1 mm

Selected chemical and physical properties of soil			
Determination	Units	Value	
pH H ₂ O	-	5.79 ± 0.07	
pH KCl	-	4.60±0.01	
EC	mS cm ⁻¹	0.21±0.09	
Sum of exchangeable alkaline cations (S)	mmol(+) kg ⁻¹ d.m.	135.0±3.3	
Hydrolytic acidity (Hh)	mmol(+) kg ⁻¹ d.m.	21.6±2.1	
Organic Carbon	g kg ^{.1} d.m.	4.20±0.10	
Total N	g kg ^{.1} d.m.	0.87 ± 0.04	
Total K	g kg ^{.1} d.m.	0.81 ± 0.08	
Total P	g kg⁻¹ d.m.	0.17 ± 0.00	
Total Cd	mg kg ^{.1} d.m.	0.22 ± 0.02	
Total Cr	mg kg ^{.1} d.m.	4.20±0.38	
Total Cu	mg kg ^{.1} d.m.	3.30 ± 0.07	
Total Ni	mg kg ^{.1} d.m.	1.96 ± 0.02	
Total Pb	mg kg ^{.1} d.m.	21.2±1.0	
Total Zn	mg kg ^{.1} d.m.	23.9±1.8	
Total Mn	mg kg ^{.1} d.m.	198±10	
Total Fe	mg kg ^{.1} d.m.	2506±6	
Sand	g kg ^{.1} d.m.	870±56	
Silt	g kg⁻¹ d.m.	80±6	
Clay	g kg⁻¹ d.m.	50 ± 4	

Each value represents the mean of three replicates \pm SD

sieved. The pH of starting materials was determined electrochemically and electrical conductivity was assessed conductometrically. The contents of nitrogen, carbon, and sulphur were determined using a CNS analyser (Vario Max Cube, Elementar). Total contents of potassium, phosphorus, and selected trace elements were determined after placing organic material samples in Teflon vessels and treating them with 6 cm³ of concentrated HNO₃ (Suprapur 65%) and 2 cm³ of H₂O₂. Then, materials were mineralised in a closed system using an AntonPaar Multiwave 3000 microwave. The total content of trace elements was determined in the control soil sample mineralised at 450°C in a chamber furnace. The contents of potassium, phosphorus, and selected trace elements in organic materials and soil were determined by inductively coupled optical emission spectrometry (ICP-OES) using a Perkin Elmer Optima 7300 DV device. The specific surface area of organic materials (S_{BET}) as well as pore volume and diameter were determined using the method described by BARRET et al. (1951).

Table 2

Determination	Units	Miscanthus straw	Biochar
pH H ₂ O	-	6.29±0.60	6.94±0.61
EC	mS cm ^{⋅1}	0.34±0.45	0.43±18
Dry matter	g kg ⁻¹	784±0.3	977±1
C _{total}		456±2	651±6
N _{total}		3.97±0.29	7.31±0.09
S _{total}	g kg⁻¹ d.m.	0.58±0.05	2.00±0.24
K _{total}		1.33±0.06	2.81 ± 0.17
P _{total}		0.73±0.04	0.94 ± 0.06
$\mathrm{Cd}_{\mathrm{total}}$		0.14±0.00	0.31±0.03
$\mathrm{Cr}_{\mathrm{total}}$	mg kg ⁻¹ d.m.	1.89±0.34	4.29±0.25
$\mathrm{Cu}_{\mathrm{total}}$		1.77±0.22	4.14 ± 0.31
Ni _{total}		0.82±0.13	1.78 ± 0.12
$\mathrm{Pb}_{\mathrm{total}}$		1.15 ± 0.18	2.44 ± 0.29
$\mathrm{Zn}_{_{\mathrm{total}}}$		14.4±4.3	32.0 ± 5.2
$\mathrm{Mn}_{\mathrm{total}}$		34.6±3.0	74.2 ± 4.5
Fe _{total}		200±48	505±68
$\mathbf{S}_{_{\mathrm{BET}}}$	$m^2 g^{-1}$	0.39±0.04	0.44 ± 0.01
Pore volume	$\mathrm{cm}^3~\mathrm{g}^{\text{-}1}$	0.0007±0.001	0.0023±0.002
Pore diameter	nm	6±1	23±3
Maximum pore diameter	nm	77	108

Chemical and physical properties of miscanthus straw and biochar

 \pm SD; n=3

The incubation analyses were carried out on 100 g soil samples supplemented with chemical substances, having effect on their acidification (AC), alkalisation (AL), and salinity (SL). The experimental design consisted of 7 treatments analysed in three replicates: 1) control soil (soil 0), 2) soil + + acidifying substances (soil+AC), 3) soil + acidifying substances + biochar (soil+AC+BC), 4) soil + alkalising substances (soil+AL), 5) soil + alkalising substances + biochar (soil+AL+BC), 6) soil + salinity substances (soil+SL), 7) soil + salinity substances + biochar (soil+SL+BC). The soil was acidified (AC) with 0.075 M H₂SO₄ and 0.15 M HNO₃ solutions (ratio 1:2). To achieve alkalisation (AL), 0.075 M Ca(OH)₂ and 0.15 M NaOH (ratio 1:2) were added to the soil. The electrical conductivity of the soil (SL) was increased by adding $CaCl_2$ and NaCl at a 1:1 molar ratio (GONET et al. 2002). The applied dose of biochar was 0.33% of the soil dry weight and was in the range outlined by the guidelines on practical aspects of biochar application to field soil in various soil management systems (Guidelines... 2010). The adopted amount to be introduced was 6.4 t C ha⁻¹.

The sample moisture content during incubation was maintained at 50% of soil water capacity. Soil samples were incubated for 210 days at 25±0.10°C

The incubated soil samples were analysed to determine the pH value potentiometrically in the soil and distilled water suspension, and in the soil and 1 M KCl solution (GONDEK, MIERZWA-HERSZTEK 2016). The sum of exchangeable alkaline cations (S) and hydrolytic acidity (Hh) were determined by the Kappen's method, as follows: (S) after 1 h extraction with 0.1 M HCl; (Hh) after 1 h extraction with 1 M CH₃COONa. Total exchangeable cations (T) and saturation with alkaline cations of the sorption complex (V) were calculated from the following relationships:

T = Hh + S,V(%) = (S / T) · 100.

Mobile trace elements were extracted for 2 h with a 1 M NH_4NO_3 solution at a room temperature (Park et al. 2011). Then, the element contents were determined in extracts using inductively coupled plasma atomic emission spectrometry (ICP-OES, Perkin Elmer Optima 7300 DV).

Statistical analysis

The experiment was carried out in triplicate. The data was analysed using Statistica 12 software (StatSoft Inc.). The mean values of analysed properties were compared using the Tukey's multiple range test at a significance level of $p \leq 0.05$. Variability within treatments was determined by calculating the standard deviation (±SD).

RESULTS

The experiment was carried out on acidic sandy soil containing 4.20 g kg⁻¹ d.m. of organic carbon and 0.87 g kg⁻¹ d.m. of total nitrogen. The total content of analysed trace elements was typical for uncontaminated soils (TOTH et al. 2008) – Table 1.

Miscanthus biochar had higher pH and electrical conductivity (EC) values than thermally untreated biomass (Table 2). In biochar, the noted levels of all analysed elements and specific surface area values were higher than in miscanthus straw.

The addition of biochar to the soil treated with acidifying substances increased the pH value, but only measured in water suspension (Table 3). In other soil treatments with alkalising (AL) and salinity (SL) substances, the introduction of biochar increased the pH value measured both in water suspension and 1 M KCl solution.

The electrical conductivity (EC) value generally did not exhibit any significant changes between individual treatments, except for the soil treated with salinity substances (Table 3). In the case of soil salinity, the addition of biochar significantly increased EC values compared to the Soil+SL treatment.

The application of biochar significantly increased the soil C content compared to the control soil as well as soil supplemented only with acidifying, alkalising, and salinity substances (Table 3). A similar tendency was observed for the soil N content (Table 3).

Table 3

Treatment	pH H ₂ O	pH KCl	EC (mS cm ⁻¹)	Total C (g kg ⁻¹ d.m.)	Total N (g kg ⁻¹ d.m.)
Soil (control)	$4.65b{\pm}0.06$	$4.45b{\pm}0.01$	0.22a±0.00	4.19 <i>a</i> ±0.11	0.400 <i>a</i> ±0.01
Soil + AC	4.42a±0.04	4.33 <i>a</i> ±0.01	$0.28a{\pm}0.02$	$4.26a{\pm}0.11$	$0.447ab{\pm}0.02$
Soil + AC + BC	$4.58b{\pm}0.02$	$4.38ab{\pm}0.02$	$0.29a{\pm}0.03$	$9.07b{\pm}0.73$	$0.473b{\pm}0.04$
Soil + AL	$5.28e{\pm}0.07$	$4.63c{\pm}0.05$	$0.23a{\pm}0.02$	$4.17a{\pm}0.25$	$0.427ab{\pm}0.02$
Soil + AL + BC	5.52 <i>f</i> ±0.02	$4.77d{\pm}0.04$	$0.25a{\pm}0.01$	$9.65b{\pm}0.97$	$0.470b{\pm}0.02$
Soil + SL	4.84c±0.03	$4.88e{\pm}0.01$	$6.37b{\pm}0.28$	4.03 <i>a</i> ±0.18	0.403 <i>a</i> ±0.01
Soil + SL + BC	$5.03d{\pm}0.04$	4.97 <i>f</i> ±0.01	$7.38c{\pm}0.86$	$9.11b{\pm}0.41$	$0.467b{\pm}0.02$

Soil pH, electrical conductivity (EC), and the C and N content

Each value represents the mean of three replicates \pm SD. The different letters within a column indicate a significant difference at $p \leq 0.05$ according to the Tukey's HSD test

The addition of BC reduced hydrolytic acidity compared to treatments with acidifying (AC) and alkalising (AL) substances. The Hh value in the Soil+AC treatment was higher than in the control soil. In the case of soils treated with salinity substances (SL), the lowest difference in Hh values (merely 0.1 mmol kg⁻¹ d.m.) was found between biochar-supplemented and non-supplemented treatments.

The sum of exchangeable alkaline cations (S) was comparable in each treatment, regardless of the dose of biochar and acidifying, alkalising, and salinity substances (Table 4). This was also reflected in the T value, which was similar in individual treatments.

Once combined with factors modifying soil properties, the application of biochar did not induce major changes in the saturation of the sorption complex with alkaline cations (V).

The analysis of mobile trace element contents in the soil supplemented with acidifying substances demonstrated their reduction after the application of biochar (Table 5). The biochar addition increased the mobility of Zn, Mn, Cu, Pb, and Cd in the soil treated with alkalising substances and elevated the contents of mobile Cu, Fe, and Ni in the soil with salinity substances.

Table 4

Treatment	Hh	S	Т	V
Treatment	(mmol kg ⁻¹ d.m.)			%
Soil (control)	$17.3c{\pm}0.5$	126.9 <i>a</i> ±7.1	144.2 <i>a</i> ±6.8	88
Soil + AC	$20.8d{\pm}0.6$	$122.7a{\pm}15.5$	$143.5a{\pm}15.6$	85
Soil + AC + BC	$19.6d{\pm}0.5$	124.0 <i>a</i> ±11.6	143.6 <i>a</i> ±12.1	86
Soil + AL	$15.5b{\pm}0.5$	$124.4a{\pm}14.3$	139.9 <i>a</i> ±14.3	89
Soil + AL + BC	$14.2ab\pm0.3$	$125.6a{\pm}13.1$	139.8 <i>a</i> ±13.2	90
Soil + SL	13.7 <i>a</i> ±0.6	129.6a±3.2	143.3 <i>a</i> ±2.5	91
Soil + SL + BC	13.6 <i>a</i> ±0.6	135.1 <i>a</i> ±10.7	148.7 <i>a</i> ±11.1	91

Properties of the soil sorption complex

Each value represents the mean of three replicates \pm SD. The different letters within a column indicate a significant difference at $p \leq 0.05$ according to the Tukey's HSD test.

Content of heavy metals extracted with $\mathrm{NH}_4\mathrm{NO}_3$				
Turneturent	Cu	Zn	Mn	Fe
Treatment	(mg kg ⁻¹ d.m.)			
Soil (control)	$0.022abc\pm 0.004$	$0.61a{\pm}0.13$	4.0 <i>a</i> ±0.4	$0.58a{\pm}0.20$
Soil + AC	$0.035c{\pm}0.004$	$0.95ab{\pm}0.04$	$23.9abc\pm1.8$	$0.35a{\pm}0.17$
Soil + AC + BC	$0.025abc{\pm}0.007$	$0.84ab{\pm}0.21$	$16.2abc\pm1.1$	0.18a±0.02
Soil + AL	0.018 <i>abc</i> ±0.004	$0.56a{\pm}0.04$	3.0a±0.2	0.38a±0.04
Soil + AL + BC	$0.013ab{\pm}0.007$	$0.74ab{\pm}0.39$	$13.6ab{\pm}1.8$	0.29a±0.12
Soil + SL	0.004 <i>a</i> ±0.001	$1.17b{\pm}0.04$	$38.3c\pm1.3$	$0.24a{\pm}0.17$
Soil + SL + BC	$0.011ab{\pm}0.001$	$1.05ab{\pm}0.10$	36.7 <i>bc</i> ±3.4	$0.55a{\pm}0.03$
Treatment	Cr	Ni	Pb	Cd
Soil (control)	0.009 <i>a</i> ±0.001	$0.044a{\pm}0.009$	0.200 <i>a</i> ±0.019	0.024 <i>a</i> ±0.004
Soil + AC	0.020a±0.003	$0.053a{\pm}0.004$	$0.443b{\pm}0.038$	$0.035abc{\pm}0.003$
Soil $+$ AC $+$ BC	$0.015a{\pm}0.007$	$0.051a{\pm}0.011$	$0.302ab{\pm}0.011$	$0.032ab{\pm}0.006$
Soil + AL	0.009 <i>a</i> ±0.001	$0.049a{\pm}0.012$	$0.129a{\pm}0.026$	0.025 <i>a</i> ±0.003
Soil + AL + BC	0.013 <i>a</i> ±0.004	$0.046a{\pm}0.022$	$0.154a{\pm}0.088$	$0.030ab{\pm}0.012$
Soil + SL	0.020a±0.000	0.032 <i>a</i> ±0.003	$0.241ab{\pm}0.031$	$0.047c\pm 0.001$
Soil + SL + BC	$0.016a{\pm}0.005$	$0.035a{\pm}0.007$	$0.225ab{\pm}0.043$	$0.044bc{\pm}0.001$

Content of heavy metals extracted with NH4NO3

Table 5

Each value represents the mean of three replicates \pm SD. The different letters within a column indicate a significant difference at $p \leq 0.05$ according to the Tukey's HSD test.

DISCUSSION

Different properties of biochar are mainly related to the type of feedstock and temperature of pyrolysis (MIERZWA-HERSZTEK et al. 2019). In general, higher pyrolysis temperature allows the transformation of aliphatic compounds into aromatic compounds; therefore, solid pyrolysis products (biochars) can have significantly different physical and chemical properties. In the present study, miscanthus biochar produced at 300°C had neutral pH (6.94). The rationale for the use of biochar produced at that temperature was the type of soil with relatively low buffer capacities and very low carbon content. Specific surface area and the macroelement content in miscanthus biochar were comparable to those determined in biochars produced from sawdust, bark, and wheat straw (GONDEK et al. 2017). The heavy metal content in miscanthus biochar was lower than that adopted for premium class biochars (GONDEK et al. 2017).

As previously mentioned, biochar, with its generally alkaline nature and substantial buffer capacity, has deacidification capabilities. However, application of this material to alkaline soils may have an opposite effect (DAI et al. 2017). In this study, the addition of biochar to soils supplemented with acidifying and alkalising substances increased the pH value. As stated by Brewer et al. (2012), the deacidifying capability of biochar can be attributed to Ca, K, Mg, Na, and Si cations which form carbonates and oxides during feedstock pyrolysis. Novak et al. (2009) demonstrated that these cations react with hydrogen and aluminium ions, thus reducing acidification, including soil exchangeable acidity. YUAN et al. (2011) and DAI et al. (2017) reported that, in addition to carbonates and oxides, functional groups, such as -COOand $-O^{-}$, which react with H⁺ in the soil, may significantly reduce acidification. Noteworthy, the direction and level of environmental changes after biochar application may vary, even despite producing biochar from the same feedstock and under the same pyrolysis conditions. This is associated with chemical composition of the feedstock obtained from soils with different levels of nutrient abundance and contamination.

Other researchers discovered that the addition of biochar is effective in improving the physical, chemical, and biological properties of saline soils (THOMAS et al. 2013). However, some studies suggested a possible increase in soil salinity after biochar application, especially in high doses (SAIFULLAH et al. 2018). In the present study, the biochar addition did not change the EC value, regardless of the substance used (AC, AL, SL). GONDEK and MIERZWA-HERSZTEK (2016) obtained different results, but they applied biochars produced from pig manure and poultry litter, which were rich in alkaline elements.

As suggested by LEI and ZHANG (2013) as well as NARTEY and ZHAO (2015), the beneficial effect of biochar on soil cationic sorption capacity should be attributed to biochar physical properties, mainly its porous struc-

ture and specific surface area. In addition, this beneficial effect of biochar on soil cationic sorption capacity was confirmed by many authors (LARID et al. 2010, FELLET et al. 2011, YUAN et al. 2011). Our study revealed no significant changes in soil sorption capacity after adding biochar to the soil supplemented with various chemical substances. GONDEK and MIERZWA-HERSZTEK (2016) obtained a substantial increase in the soil CEC value after applying biochars from pig manure and poultry litter. However, it should be noted that these authors used in their study different materials for biochar production as well as higher doses thereof.

The mobility and bioavailability of heavy metals in the environment depends on both: their total concentration and their binding in the soil solid phase (Acosta et al. 2011). The latter is modified by sorption, desorption, precipitation, and dissolution processes. As reported by PARK et al. (2011), USMAN et al. (2013), and AHMAD et al. (2014), immobilisation of heavy metals in biochar-supplemented soil may be attributed to several chemical processes, e.g. ion exchange, chemical sorption, and complexation on the biochar surface. PARK et al. (2011) and USMAN et al. (2013) found that immobilisation of heavy metals can result from precipitation with biochar-originating mineral components, such as carbonates, silicates, and phosphates or from processes caused by their application. Biochars can also limit the mobility of heavy metals by changing the redox potential, as reported by CHOPPALA et al. (2012). These authors focused on the effect of biochar addition to soil on transformations of Cr^{+6} into Cr^{+3} . The relative contribution of individual mechanisms to immobilisation of heavy metals after biochar application remains unknown. However, some authors, such as HOUBEN et al. (2013), have suggested that a change in soil pH is a decisive factor here.

The content of mobile trace elements is also determined by the soil pH, sorption capacity, and salt content. Other authors demonstrated that the addition of biochar to soil may decrease the mobility of trace elements by reducing soil acidification (LUCCHINI et al. 2014). Our study revealed different effects of biochar addition on the contents of analysed mobile trace elements, depending on substances applied to alter soil chemical properties (AC, AL, SL). The best effect on reducing the mobility of trace elements was produced by biochar added to the soil with acidifying substances. In the case of soil alkalisation and salinity, the effect of biochar application was less visible. Therefore, it should be emphasised that the limited mobility of trace elements in soil after its supplementation with biochar results not only from the formation of poorly soluble heavy metal compounds in soil through its reduced acidification. The highly porous biochar structure and the presence of functional groups certainly have an equally significant effect on heavy metal adsorption (LIU, ZHANG 2009).

In their previous studies, Gondek and MIERZWA-HERSZTEK (2016) discovered a significant reduction in the mobility of Cu (28% to 69%), Cd (77% to 100%), Pb (94% to 99%), and Zn (15% to 97%) in soil, depending on the

biochar type and dose. Undoubtedly, this resulted from the significant increase in soil pH after biochar application. According to these authors, the reduced acidification resulted in the formation of poorly soluble heavy metal compounds in the soil. However, it should be noted that this was probably not only due to the alkalising effect of the materials applied. It should also be emphasised that the highly porous structure of biochar and the presence of functional groups certainly had a significant impact on the adsorption of heavy metals (LIU, ZHANG 2009). Similarly, Fellet et al. (2011) demonstrated that the application of biochar reduced the mobility of Cd, Pb, and Zn. Biochar application can cause transformations of easily accessible forms of heavy metals into chemically stable forms, which, in turn, reduces their mobility and bioavailability (AHMAD et al. 2014a). As stated by PARK et al. (2011), USMAN et al. (2013) and AHMAD et al. (2014b), the immobilisation of heavy metals in the soil enriched with biochar can be attributed to several chemical processes, including ion exchange, chemical sorption, and surface complexation.

GONDEK and MIERZWA-HERSZTEK (2016) argued that the biochar addition to the soil did not cause any targeted changes of iron mobility; however, it significantly reduced the Mn mobility because of the deacidifying effect of materials used. According to AL-WABEL et al. (2015), the addition of biochar to soil has effect on the content of both available iron and manganese.

As stated by ALABOUDI et al. (2019), the Cr mobility is increased after applying biochar to soil. According to these authors, the increasing trend of bioavailable Cr can be attributed to the increase of soil pH due to biochar addition. Cr(III) can be oxidised to Cr(VI) by manganese oxides and/or alkaline resources (such as biochar) that increase soil pH above neutral. Therefore, the Cr increase in soil is a function of increasing soil pH.

CONCLUSIONS

1. Regardless of the form of soil chemical degradation, the addition of biochar generally increased the soil pH value compared to treatments with no biochar added.

2. Regardless of the form of soil chemical degradation, the application of biochar did not alter the EC value under experimental conditions, and the contents of C and N resulted from their introduction together with biochar.

3. The biochar addition to soils subjected to various chemical degradations generally reduced the hydrolytic acidity but did not change the content of alkaline cations and soil sorption capacity.

4. The best effect on reducing the mobility of trace elements was achieved by adding biochar to the soil supplemented with acidifying substances.

REFERENCES

- ACOSTA J.A., JANSEN B., KALBITS K., FAZ A., MARTINEZ-MARTINEZ S. 2011. Salinity increase mobility of heavy metals in soil. Chemosphere, 85: 1318-1324. DOI: 10.1016/j.chemosphere.2011.07.046
- AHMAD M., RAJAPAKSHA A.U., LIM J.E., ZHANG M., BOLAND N., MOHAN D., VITHANAGE M., LEE S.S., OK Y.S. 2014. Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere, 99: 19–33. DOI: 10.1016/j.chemosphere.2013.10.071
- AHMAD M., LEE S.S., LIM J.E., LEE S.-E., CHO J.S., MOON D.H., HASHIMOTO Y., OK Y.S. 2014a. Speciation and phytoavailability of lead and antimony in a small arms range soil amended with mussel shell, cow bone and biochar: EXAFS spectroscopy and chemical extractions. Chemosphere, 95: 433-441. DOI: 10.1016/j.chemosphere.2013.09.077
- AHMAD M., RAJAPAKSHA A.U., LIM J.E., ZHANG M., BOLAN N., MOHAN D., VITHANAGE M., LEE S.S., OK Y.S., 2014b. Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere, 99: 19-33. DOI: 10.1016/j.chemosphere.2013.10.071
- ALABAUDI K.A., AHMED B., BRODIE G. 2019. Effect of biochar on Pb, Cd and Cr availability and maize growth in artificial contaminated soil. Ann. Agric. Sci., 64: 95-102. DOI: 10.1016/j. aoas.2019.04.002
- AL-WABEL M.I., USMAN A.R.A., EL-NAGGAR A.H., ALY A.A., IBRAHIM H.M., ELMAGHRABY S., AL-OMRAN A. 2015. Conocarpus biochar as a soil amendment for reducing heavy metal availability and uptake by maize plants. Saudi J. Biol. Sci., 22: 503-511. DOI: 10.1016/j. sjbs.2014.12.003
- ATKINSON C.J., FITZGERALD J.D., HIPPS N.A. 2010. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soil: a review. Plant Soil, 337(1): 1-18. DOI: 10.1007/s11104-010-0464-5
- BARRET E.P., JOYNER L.G., HALENDA P.H. 1951. The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. J. Amer. Chem. Soc., 73(1): 373-380. DOI: 10.1021/ja01145a126
- BISWAS B., QI F., BISWAS J.K., WIJAYAWARDENA A., KHAN M.A.I., NAIDU R. 2018. The fate of chemical pollutants with soil properties and processes in the climate change paradigm – a review. Soil Syst., 2(51): 1-20. DOI: 10.3390/soilsystems2030051
- BREWER C.E., HU Y.Y., SCHMIDT-ROHR K., LOYNACHAN T.E., LAIRD D.A., BROWN R.C. 2012. Extent of pyrolysis impacts on fast pyrolysis biochar properties. J. Environ. Qual., 41: 1115-1122. DOI: 10.2134/jeq2011.0118
- CHENG C.H., LEHMANN J., THIES J.E., BURTON S.D., ENGELHARD M.H. 2006. Oxidation of black carbon by biotic and abiotic processes. Org. Geochem., 37: 1477-1488. DOI: 10.1016/j.orggeochem. 2006.06.022
- CHOPPALA G.K., BOLAN N.S., MEGHARAJ M., CHEN Z., NAIDU R. 2012. The influence of biochar and black carbon on reduction and bioavailability of chromate in soils. J. Environ. Qual., 41: 1175-1184. DOI: 10.2134/jeq2011.0145
- DAI Z., ZHANG X., TANG C., MUHAMMAD N., WU J., BROOKES P.C., XU J. 2017. Potential role of biochars in decreasing soil acidification – a critical review. Sci. Tot. Environ., 581-582: 601-611. DOI: 10.1016/j.scitotenv.2016.12.169
- FELLET G., MARCHIOL L., DELLE VEDOVE G., PERESSOTTI A. 2011. Application of biochar on mine tailings: Effects and perspectives for land reclamation. Chemosphere, 83: 1262-1267. DOI: 10.1016/j.chemosphere.2011.03.053
- FILIPEK T., SKOWROŃSKA M. 2013. Current dominant causes and effects of acidification of soils under agricultural use in Poland. Acta Agroph., 20(2): 283-294.
- GAI X., WANG H., LIU J., ZHAI L., LIU S., REN T., LIU H. 2014. Effect of feedstock and pyrolysis temperature on biochar adsorption of ammonium and nitrate. PLoS One, 9(12): 1-19. DOI: 10.1371/journal.pone.0113888
- GONDEK K., MIERZWA-HERSZTEK M. 2016. Effect of low-temperature biochar derived from pig

manure and poultry litter on mobile and organic matter-bound forms of Cu, Cd, Pb and Zn in sandy soil. Soil Use Manage., 32: 357-367. DOI: 10.1111/sum.12285

- GONDEK K., MIERZWA-HERSZTEK M. 2016. Effect of thermal conversion of pig manure and poultry litter on the content and mobility of Mn and Fe in biochars and in soil after their application. Chilean J. Agric. Res., 73(3): 349-355. 10.4067/S0718-58392016000300013
- GONDEK K., MIERZWA-HERSZTEK M., BARAN A., SZOSTEK M., PIENIĄŻEK R., PIENIĄŻEK M., STANEK--TARKOWSKA J., NOGA T. 2017. The effect of low-temperature conversion of plant materials on the chemical composition and ecotoxicity of biochars. Waste Biomass Valor., 8: 599-609. DOI: 10.1007/s12649-016-9621-2
- GONET S.S., DEBSKA B., PAKUŁA J. 2002. The content of soluble organic carbon in soils and organic fertilizers. Eds. PTSH Wroclaw, pp. 76.
- Guidelines for biochar application to soil International Biochar Initiative. 2010. www.biocharinternational.org
- HOUBEN D., EVRARD L., SONNET P. 2013. Mobility, bioavailability and pH-dependent leaching of cadmium, zinc and lead in a contaminated soil amended with biochar. Chemosphere, 92: 1450-1457. DOI: 10.1016/j.chemosphere.2013.03.055
- IBI. 2012. Standardized product definition and product testing guidelines for biochar that is used in soil. (cited 14 March 2019)
- INAL A., GUNES A., SAHIN O., TASKIN M.B., KAYA E.C. 2015. Impacts of biochar and processed poultry manure, applied to a calcareous soil, on the growth of bean and maize. Soil Use Manage., 31: 106-113. DOI: 10.1111/sum.12162
- KOOKANA R.S., SARMAH A.K., VAN ZWIETEN L., KRULL E., SINGH B. 2011. Biochar application to soil: agronomic and environmental benefits and unintended consequences. Donald LS (eds.) Adv. Agronom., 112: 103-143. DOI: 10.1016/B978-0-12-385538-1.00003-2
- LAIRD D.A., FLEMING P., DAVIS D.D., HORTON R., WANG B., KARLEN D.L. 2010. Impact of biochar amendments on the quality of a typical midwestern agricultural soil. Geoderma, 158: 443-449. DOI: 10.1016/j.geoderma.2010.05.013
- Lee HW, Kim Y-M, Kim S, Ruy Ch, Park SH, Park Y-K. 2018. Review of the use of activated biochar for energy and environmental applications. Carbon Letters, 26(1):1-10.
- LEI Q., ZHANG R. 2013. Effects of biochars derived from different feedstocks and pyrolysis temperatures on soil physical and hydraulic properties. J. Soils Sediment, 13: 1561-1572. DOI: 10.1007/s11368-013-0738-7
- LIU X.H., ZHANG X.C. 2012. Effect of biochar on pH of alkaline soils in the loess plateau: results from incubation experiments. Int J Agric Biol., 14: 745-750.
- LIU Z., ZHANG F.S. 2009. Removal of lead from water using biochars prepared from hydrothermal liquefaction of biomass. J Hazard Mater., 167: 933-939. DOI: 10.1016/j.jhazmat. 2009.01.085
- LU H., ZHANG W., WANG S., ZHUANG L., YANG Y., QIU R. 2013. Characterization of sewage sludge -derived biochars from different feedstocks and pyrolysis temperatures. J. Anal. Appl. Pyrol., 102: 137-143. DOI: 10.1016/j.jaap.2013.03.004
- LUCCHINI P., QUILLIAM R.S., DELUCA T.H., VAMERALI T., JONES D.L. 2014. Does biochar application alter heavy metal dynamics in agricultural soil? Agric. Ecosyst. Environ., 184: 149-157. DOI: 10.1016/j.agee.2013.11.018
- MIERZWA-HERSZTEK M., GONDEK K., NAWROCKA A., PIŃKOWSKA H., BAJDA T., STANEK-TARKOWSKA J., SZOSTEK M. 2019. FT-IR analysis and the content of phenolic compounds in exogenous organic matter produced from plant biomass. J. Elem., 24(3): 879-896. DOI: 10.5601/jelem.2018. 23.3.1716
- NARTEY O.D., ZHAO B. 2014. Biochar preparation, characterization, and adsorptive capacity and its effect on bioavailability of contaminants: an overview. Adv. Mater. Sci. Eng., ID 715398, pp.12. DOI: 10.1155/2014/715398
- NOVAK J.M., BUSSCHER W.J., LAIRD D.L., AHMEDNA M., WATTS D.W., NIANDOU M.A.S. 2009. Impact

of biochar amendment on fertility of a southeastern coastal plain soil. Soil Sci., 174: 105-112. DOI: 10.1097/SS.0b013e3181981d9a

- PARK J.H., CHOPPALA G.K., BOLAN N.S., CHUNG J.W., CHUSAVATHI T. 2011. Biochar reduces the bioavailability and phytotoxicity of heavy metals. Plant Soil, 348: 439-451. DOI: 10.1007/ /s11104-011-0948-y
- RASSE D.P., BUDAI A., O'TOOLE A., MA X., RUMPEL C., ABIVEN S. 2017. Persistence in soil of Miscanthus biochar in laboratory and field conditions. PLoS ONE, 12(9):e0184383. DOI:10.1371/journal.pone.0184383
- SAIFULLAH, DAHLAWI S., NAEEM A., RENGEL Z., NAIDU R. 2018. Biochar application for the remediation of salt-affected soils: Challenges and opportunities. Sci Total Environ., 625: 320-335. DOI: 10.1016/j.scitotenv.2017.12.257
- SOLAIMAN Z.N., ANAWAR H.M. 2015. Application of biochars for soil constraints: challenge and solutions. Pedosphere, 25(5): 631-638. DOI: 10.1016/S1002-0160(15)30044-8
- THOMAS S.C., FRYE S., GALE N., GARMON M., LAUNCHBURY R., MACHADO N., MELAMED S., MURRAY J., PETROFF A., WINSBOROUGH C. 2013. Biochar mitigates negative effects of salt additions on two herbaceous plant species. J. Environ. Manage., 129: 62-68. DOI: 10.1016/j.jenvman.2013.05.057
- TÓTH G., MONTANARELLA L., RUSCO E. 2008. Threats to soil quality in Europe. Scientific and technical reports. European Commission Joint Research Centre Institute for Environment and Sustainability, pp. 150. DOI:10.2788/8647
- USMAN A.R.A., SALLAM A.S., AL-OMRAN A., EL-NAGGAR A.H., ALENAZI K.K.H., NADEEM M., AL-WABEL M.I. 2013. Chemically modified biochar produced from conocarpus wastes: an efficient sorbent for Fe(II) removal from acidic aqueous solutions. Adsorpt. Sci. Technol. 31: 625-640. DOI: 10.1260/0263-6174.31.7.625
- WIDLAK M. 2016. Natural indicator of soil salinity. Proceedings of ECOpole, 10(1): 359-365.
- WU W., YANG M., FENG Q., MCGROUTHER K., WANG H., LU H., CHEN Y. 2012. Chemical characterization of rice straw-derived biochar for soil amendment. Biom. Bioener., 47: 268-276. DOI: 10.1016/j.biombioe.2012.09.034
- YUAN J., XU R., WANG N., LI J. 2011. Amendment of acid soils with crop residues and biochars. Pedosphere, 21: 302-308. DOI: 10.1016/S1002-0160(11)60130-6
- YUAN J.H., XU R.K. 2011. The amelioration effects of low temperature biochar generated from nine crop residues on an acidic ultisol. Soil Use Manage., 27: 110-115. DOI: 10.1111/j.1475-2743. 2010.00317.x
- ZHANG D., YAN M., NIU Y., LIU X., VAN ZWIETEN L., CHEN D., BIAN R., CHENG K., LI L., JOSEPH S., ZHENG J., ZHANG X., ZHENG J., CROWLEY D., FILLEY T.R., PAN G. 2016. Is current biochar research addressing global soil constraints for sustainable agriculture? Agr. Ecosyst. Environ., 226: 25-32. DOI: 10.1016/j.agee.2016.04.010
- ZHAO L., CAO X., MAŠEK O., ZIMMERMAN A. 2013. Heterogeneity of biochar properties as a function of feedstock sources and production temperatures. J. Hazard Mater., 256-257: 1-9. DOI: 10.1016/j.jhazmat.2013.04.015