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

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ABSTRACT

By-products of animal breeding and raising can contain considerable amounts of trace elements, including Mn and Fe, due to the fact that their amounts in fodders are purposefully being increased. Thermal conversion of pig manure and poultry litter may have a significant effect on changes in the content and mobility of Mn and Fe in these materials. The aim of the research was to evaluate the 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 (0.5%, 1%, and 2% amendments to the soil). As a result of thermal conversion of pig manure and poultry litter, an increase in the content of total forms and a reduction of Mn and Fe forms extracted with water were recorded. The 2% amendment of pig manure biochar to soil caused an increase in the content of mobile forms of Fe, whereas poultry litter biochar decreased mobility of this element. Introduction of pig manure biochar and poultry litter biochar to the soil caused a similar immobilization of mobile forms of Mn as in the case of application of thermally unprocessed manure and litter. It has been shown that the content of Fe and Mn extracted with 0.025 M $C_{10}H_{22}N_4O_8$ was higher than the content of these elements extracted with 1 M NH_4NO_3.

Key words: Biochar, iron, manganese, pig manure, poultry litter, soil.

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INTRODUCTION

Chemical composition of biochars is significantly varied and depends on the chemical composition of biomass used for their production and on conditions of the thermal conversion process (Enders et al., 2012). In terms of chemical composition, biochars differ not only among themselves, but from other types of organic matter (OM). The difference is that they contain much higher amounts of aromatic C compounds. Biochar also contains a mineral fraction composed of macroelements and trace elements which are important for using these materials for fertilizing purposes (Lehmann et al., 2011). Due to technological parameters of the thermal conversion process, especially temperature, one can obtain products that differ not only in physical properties, but also in the content of substances which are easily decomposed in soil conditions (Jindo et al., 2014). By-products of animal breeding and raising can contain considerable amounts of trace elements, including Mn and Fe, due to the fact that their amounts in fodders are purposefully being increased (Commission Regulation, 2003). Under conditions of thermal conversion of manure and poultry litter, it is possible to increase the content and mobility of Mn and Fe. On one hand, it results from loss of OM (compaction effect). On the other hand, it is caused by degradation of various compounds and formation of new or activation of initially unavailable chemically bound substances or elements (Al-Wabel et al., 2013).

Total content of Mn and Fe in soils is high and may reach several percent in the case of Fe. These elements are used by plants in small amounts (Walna et al., 2010). In the soil environment, Mn and Fe form numerous compounds and their bioavailability is conditioned by soil properties, mainly by the redox potential and pH (Xue et al., 2006). According to Livens (1991), Mn and Fe, which can be found in topsoils, can form complex bonds with OM and remain available for plants in this form. This theory is confirmed by results of research conducted by Kobierski (2004), where the highest amounts of Mn and Fe forms extracted with DTPA were determined in topsoils. Xue et al. (2006) point to the existence of a relationship between Fe and the OM content, while at the same time stressing the possibility that this phenomenon may be intensified as a result of OM accumulation in soil. The cited authors do not, however, point to a connection between OM and Mn ions.

Taking into account a multitude of trace elements occurring in soil, more and more attention is being focused on the ones with the highest impact on the environment, in other words: Cd, Pb, Cu, and Zn. Manganese and Fe have a slightly weaker negative effect on the environment. That is why there are few papers

concerning the content and bioavailability of these elements. However, determination of the content and mobility of Mn and Fe in soil may provide information on the effect of some anthropogenic elements on the natural environment. It should also be remembered that both of these elements are extremely important in terms of influencing the bioavailability of other trace metals (Samsuri et al., 2013).

Considering the physical properties of biochar as well as considerable OM content, this material more and more often is used as a sorbent and reservoir of mineral substances (Ahmad et al., 2014a; 2014b). Thermal conversion of pig manure and poultry litter may have a significant effect on changes in the content and mobility of Mn and Fe in these materials. However, functional groups which are present on the surface of biochar can "control" the content of mobile forms of trace elements in these materials and in soil by forming specific complexes (Han et al., 2013). One can therefore expect a beneficial effect of biochar on the process of stabilization of mobile forms of Mn and Fe in soil. Therefore the aim of this research was to evaluate the 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.

MATERIAL AND METHODS

Soil and amendments collection
The research was conducted on soil which had a natural content of Mn and Fe collected from a 0-20 cm layer from an area of southern Poland. Properties of the soil used in the research are presented in Table 1.

Thermal conversion of pig manure (PM) and poultry litter (PL) was conducted in laboratory conditions, at a station designed for thermal conversion of biomass at reduced air access (1%-2%) (IBI, 2012). Temperature inside the combustion chamber was 300 ± 10 °C. The exposure time was 15 min. The speed of heating of the combustion chamber was 10 °C min^{-1}. Selection of time and temperature of pyrolysis was done according to our preliminary research and results of other authors' research (Al-Wabel et al., 2013; Gondek et al., 2014).

Chemical analysis of soil
Mobile forms of Mn and Fe were extracted from the soil with 1 M NH_4NO_3 solution (soil:solution = 1:2.5) for

Table 1. Selected chemical and physical properties of soil.

pH H_2O	5.79 ± 0.07
pH KCl	4.60 ± 0.01
Electrical conductivity, $\mu S\ cm^{-1}$	21.0 ± 9.0
Total C, %	0.42 ± 0.01
Total N, %	0.087 ± 0.004
Total Mn, mg kg^{-1}	198 ± 10
Total Fe, mg kg^{-1}	2515 ± 6
Sand, g kg^{-1}	870 ± 56
Silt, g kg^{-1}	80 ± 6
Clay, g kg^{-1}	50 ± 4

Each value represents the mean of three replicates ± standard deviation.

2 h (Park et al., 2011). Content of the studied metals in bonds with OM was determined using sequential chemical extraction developed by Zeien and Brümmer (1989) in which forms joined in bonds with OM were extracted with 0.025 M $C_{10}H_{22}N_4O_8$ solution, pH = 4.6 (soil:solution = 1:25) for 90 min.

The extraction force of NH_4NO_3 is comparable to the ability of plants to take up trace elements from the soil solution. The use of $C_{10}H_{22}N_4O_8$ (as the next extractant in the chemical extraction sequence) makes it possible to determine the content of organic matter-bound forms of trace elements. Since the complex organic component is likely to be degraded (as a result of mineralization), determination of this fraction of trace elements may increase the pool of heavy metals available for plants in soil. As stated by Al-Wabel et al. (2015), the analysis made with the use of such extractants is a reliable test for examining the actual and potential bioavailability of heavy metals for plants.

Chemical analysis of amendments
In order to characterize the properties of PM, biochar produced from pig manure (PMB), PL as well as of biochar produced from poultry litter (PLB), all of which were used in the research, the materials were ground in a laboratory mill (with a 1 mm screen), and then dried at 105 °C for 12 h (Jindo et al., 2012) and subjected to analyses. The pH of the materials (material:water = 1:5) was determined electrochemically using a pH meter (pH-Meter CP–505, Elmetron Sp.jul., Zabrze), electrical conductivity (EC; material:water = 1:5) was determined using a conductivity meter (CCO-501 Conductivity/Oxygen meter, Hotek Technologies, Tacoma, Washington, USA) (Meier et al., 2015), and content of total forms of N, C, and S was determined on analyzer (vario MAX cube CNS, Elementar Analysensysteme GmbH, Hanau, Germany). The total contents of Mn and Fe were determined after incinerating the sample in a chamber furnace at 450 °C for 12 h and mineralization of the residue in a mixture of concentrated nitric and perchloric acid (3:2) (v/v). The content of bioavailable forms in organic materials was determined after a 24-h extraction (at room temperature) of the sample with redistilled water (material:water = 1:5) (Gondek et al., 2014). Concentration of the studied elements in the obtained solutions was determined by inductively coupled plasma optical emission spectrometry (Optima 7300 DV, ICP-OES spectrometers, Perkin Elmer, Waltham, Massachusetts, USA) (Oleszczuk et al., 2007). Specific surface area of organic materials as well as size and volume of pores were determined using an Accelerated Surface Area and Porosimetry Analyzer (ASAP 2010, Micromeritics Instrument Corporation, Norcross, Georgia, USA). Specific surface area was determined using physical adsorption of N at liquid nitrogen temperature (77 °K) from the Brunauer-Emmet-Teller (S_{BET}) equation. Prior to measurement (S_{BET}), studied samples were subjected to desorption at 105 °C in vacuum and rinsed with pure He. Sample degassing time was 16 h. The surface degassing state was controlled in automatic mode (Barrett et al., 1951).

Incubation study of soil, experimental design and analysis

Incubation tests were carried out in 100 g analytical samples of soil amended with 0.5%, 1%, and 2% of the above-mentioned organic materials: PM, PMB, PL, PLB. Moisture of a sample was maintained at 60% of soil water capacity. The control sample was kept without amendment of organic materials. The soil samples were incubated for 150 d at 25 ± 0.10 °C. The following were determined in the samples after incubation: soil pH – potentiometrically in a soil and water suspension and in a suspension of the soil and 1 M KCl solution (soil:solution = 1:2.5); EC – by conductometer; and cation exchange capacity (CEC) by Kappen method (Jaremko and Kalembasa, 2014).

Statistical analysis

The experiment was done in triplicate. The obtained data were elaborated by means of STATISTICA 12 software (StatSoft, Tulsa, Oklahoma, USA). Mean values of the analyzed properties were compared using a multiple Duncan test at the significance level of p ≤ 0.05. Variation within treatments was determined by calculating the values of standard deviation (± SD).

RESULTS AND DISCUSSION

Incubation study

Sandy acid soil containing 198 mg Mn kg^{-1} DM and 2515 mg Fe kg^{-1} DM was used for the research. The total C content and total N content amounted to 0.42% and 0.087%, respectively (Table 1). The application of organic materials caused an increase in the contents of total C and N compared to the control soil (Table 2). The contents of both studied elements increased in line with the amendment of organic material to the soil. The value of C:N ratio for non-converted organic materials PM and PL applied into the soil was reduced with an increase in the amendment. An inverse relationship was observed for biochars BPM and BPL.

Chemical characterization

Pig manure (PM) and PL had lower pH values and lower values of electrical conductivity (EC) in comparison to biochars obtained from these materials PMB and PLB

Table 2. Content of total C, total N, and ratio C:N in soil after incubation.

Treatment	C$_{TOT}$	N$_{TOT}$	C:N
		%	
Soil	0.43 ± 0.05a	0.054 ± 0.002a	7.90 ± 0.90abcd
Soil + PM 0.5%	0.56 ± 0.01cd	0.065 ± 0.003b	8.70 ± 0.39de
Soil + PM 1%	0.61 ± 0.02de	0.075 ± 0.001de	8.16 ± 0.17cd
Soil + PM 2%	0.86 ± 0.07g	0.103 ± 0.006g	8.36 ± 0.24de
Soil + BPM 0.5%	0.58 ± 0.03cde	0.073 ± 0.011cde	8.01 ± 0.78bcd
Soil + BPM 1%	0.76 ± 0.01f	0.090 ± 0.001f	8.49 ± 0.09de
Soil + BPM 2%	1.04 ± 0.03h	0.115 ± 0.002h	9.10 ± 0.26e
Soil + PL 0.5%	0.48 ± 0.01ab	0.066 ± 0.003bc	7.29 ± 0.33ab
Soil + PL 1%	0.54 ± 0.03bc	0.072 ± 0.006bcde	7.48 ± 0.27abc
Soil + PL 2%	0.71 ± 0.04f	0.099 ± 0.004g	7.14 ± 0.35a
Soil + BPL 0.5%	0.57 ± 0.02cd	0.069 ± 0.004bcd	8.24 ± 0.25cd
Soil + BPL 1%	0.64 ± 0.03e	0.079 ± 0.003e	8.15 ± 0.32cd
Soil + BPL 2%	0.85 ± 0.04g	0.099 ± 0.003g	8.64 ± 0.63de

Each value represents the mean of three replicates ± standard deviation. The different letters within a column indicate a significant difference at p ≤ 0.05 according to Duncan's multiple range tests.
PM: Pig manure, PL: poultry litter, PMB: pig manure biochar, PLB: poultry litter biochar.

(Table 3). The pig manure biochar (PMB) and PLB were found to have higher total N, C, and S contents as well as higher specific surface area (S$_{BET}$) as compared to materials not subjected to pyrolysis. Similar S$_{BET}$ for PL produced at 350 °C was obtained by Novak et al. (2009). Thermal conversion of PL and PM also led to an increase in pore diameter. Compared to PMB, pore volume of PLB was higher by 38%, while pore diameter, lower by 14%.

Manganese and iron content in pig manure and in biochar

Manganese content in the PM was lower than in PL (Table 4). The determined content of total forms of Mn in biochars was significantly higher. The increase in Mn content in relation to PM was more than 50% in the case of PMB, and more than 37% in the case of PL and PLB. As a result of thermal conversion of PM and PL, a reduction in the content of Mn forms extracted with water was observed. The content of total forms of Fe in the studied materials was higher than the determined Mn content (Table 4). Relatively greater amounts of available forms of this element were extracted from organic materials. A similar tendency as in the case of Mn was observed, namely a tendency of increasing content of total forms of Fe as a result of thermal conversion of PM and PL, and of reducing Fe forms extracted with water in

Table 3. Selected properties of organic materials.

Properties	Pig manure	Pig manure derived biochar	Poultry litter	Poultry litter derived biochar
Dry matter, %	17.8 ± 0.1	97.9 ± 0.2	32.3 ± 1.7	98.6 ± 0.2
pH (H$_2$O)	7.56 ± 0.01	8.32 ± 0.00	7.53 ± 0.02	8.41 ± 0.02
Electric conductivity, μS·cm^{-1}	20.3 ± 3.6	77.7 ± 17.8	49.1 ± 12.4	91.5 ± 2.6
Total N, %	3.14 ± 0.04	3.49 ± 0.05	2.51 ± 0.17	3.27 ± 0.07
Total C, %	37.0 ± 0.3	39.8 ± 0.6	32.3 ± 0.3	37.7 ± 0.3
Total S, %	0.47 ± 0.02	0.36 ± 0.05	0.16 ± 0.02	0.18 ± 0.02
Specific surface area (S$_{BET}$), m^2 g^{-1}	1.62 ± 0.10	2.05 ± 0.19	1.83 ± 0.22	2.76 ± 0.29
Pore volume, cm^3 g^{-1}	0.007 ± 0.000	0.008 ± 0.001	0.006 ± 0.000	0.011 ± 0.002
Pore diameter, nm	15 ± 1	21 ± 3	14 ± 2	18 ± 3

Each value represents the mean of three replicates ± standard deviation.
S$_{BET}$: Specific surface area determined by Brunauer-Emmet-Teller equation.

Table 4. Manganese and iron content in pig manure, poultry litter, and biochars.

Content	Pig manure	Pig manure derived biochar	Poultry litter	Poultry litter derived biochar
Total Mn, mg kg^{-1}	214 ± 17	321 ± 15	351 ± 33	482 ± 79
Mn-H$_2$O, mg kg^{-1}	6.19 ± 0.58	2.69 ± 0.27	5.28 ± 0.30	1.16 ± 0.00
Mn-H$_2$O in total Mn, %	2.83	0.83	1.50	0.24
Total Fe, mg kg^{-1}	2754 ± 272	7412 ± 656	1052 ± 60	1611 ± 214
Fe-H$_2$O, mg kg^{-1}	142 ± 7	11.0 ± 0.7	74.8 ± 11	6.6 ± 0.6
Fe-H$_2$O in total Fe, %	5.15	0.14	7.11	0.40

Each value represents the mean of three replicates ± standard deviation.

PMB and PLB. Results obtained by Hossain et al. (2011) indicate that the content of trace elements increases during pyrolysis, depending on the used temperature, which corresponds with mass loss. In the conducted research, the temperature used (300 °C) also caused an increase in the content of total forms of Mn and Fe and a reduction in the content of Mn and Fe forms extracted with water. According to He et al. (2010), pyrolysis temperature above 350 °C leads to higher stability of trace element forms. On the other hand, according to Song and Guo (2012), suggested temperature, for agricultural purposes, of pyrolysis of materials should be approximately 300 °C.

Soil pH, EC, and cation exchange capacity (CEC)

The pH values determined in the soil and water suspension and in the suspension of the soil and KCl solution depended on the type and quantity of the applied material (Table 5). Application of organic materials caused considerable reduction of soil acidification. Increasing the addition of organic material to the soil brought about greater and greater increases in pH, determined both in the soil and water suspension and in the suspension of the soil and KCl solution. When comparing the effect of PM and PL with biochars (PMB, PLB) produced from these materials, a significantly

Table 5. Soil pH, electrical conductivity (EC), and cation exchange capacity (CEC).

Treatment	pH (H$_2$O)	pH (KCl)	EC	CEC
			μS cm^{-1}	mmol kg^{-1}
Soil	5.04 ± 0.03a	4.46 ± 0.01a	146 ± 34a	89 ± 3a
Soil + PM 0.5%	5.60 ± 0.04b	4.87 ± 0.02b	389 ± 14abc	93 ± 3ab
Soil + PM 1%	5.88 ± 0.04c	5.27 ± 0.06c	649 ± 22cde	101 ± 3ab
Soil + PM 2%	6.41 ± 0.05e	6.07 ± 0.11e	992 ± 17g	108 ± 4bc
Soil + BPM 0.5%	6.07 ± 0.05d	5.45 ± 0.03d	369 ± 84ab	93 ± 5ab
Soil + BPM 1%	6.47 ± 0.03f	6.08 ± 0.05e	574 ± 58bcde	103 ± 8ab
Soil + BPM 2%	7.09 ± 0.02h	6.79 ± 0.02g	799 ± 158efg	120 ± 1c
Soil + PL 0.5%	5.94 ± 0.05c	5.36 ± 0.03cd	505 ± 11cd	100 ± 7ab
Soil + PL 1%	6.37 ± 0.00e	6.07 ± 0.02e	726 ± 9def	105 ± 4bc
Soil + PL 2%	6.83 ± 0.00g	6.72 ± 0.01g	941 ± 343fg	137 ± 11d
Soil + BPL 0.5%	6.57 ± 0.01f	6.21 ± 0.04f	443 ± 33bc	98 ± 2ab
Soil + BPL 1%	7.10 ± 0.03h	6.95 ± 0.10h	434 ± 65bc	119 ± 2c
Soil + BPL 2%	7.60 ± 0.02i	7.41 ± 0.01i	569 ± 82bcde	170 ± 7e

Each value represents the mean of three replicates ± standard deviation. The different letters within a column indicate a significant difference at p ≤ 0.05 according to Duncan's multiple range tests.
PM: Pig manure, PL: poultry litter, PMB: pig manure biochar, PLB: poultry litter biochar.

greater deacidifying effect of biochars was determined. The best results of the deacidifying effect were obtained after application of 1% and 2% amendment of biochars. This effect is due to a higher content of organic matter generates more output of alkali oxides which hydrolyze generate OH groups that increase the pH values (Lehmann et al., 2011; Inal et al., 2015). The results of our research confirm the observations made by Yuan et al. (2011), according to which alkaline substances are easier released from biochars than from materials which have not been subjected to thermal conversion. The process of thermal conversion brings about considerable changes in the chemism of biochars. Loss of compounds which are organic in nature in favor of mineral bonds takes place, which show greater potential for soil deacidification (Yuan et al., 2011). Moreover, the content of carbonates as well as of Ca and Mg cations (which are easily transferred into soil solution) increases (Van Zwieten et al., 2010). According to Cheng et al. (2006), application of biochar to soils may contribute to the release of acidifying substances as a result of chemical and microbiological processes taking place. Research results obtained by Liu and Zhang (2012) confirm the probability of occurrence of such a situation in a short period of time (4-mo after application). Inal et al. (2015) also report that application of PLB led to a reduction of pH in the alkaline soil. According to Liu and Zhang (2012), this may be caused by a release of functional groups of acidic character during oxidation of biochar. According to Atkinson et al. (2010), binding of Ca to P may take place in such conditions, which in consequence reduces the concentration of Ca ions in a soil solution.

Relatively to the quantity of materials used (0.5%, 1%, 2%), the value of soil EC increased (Table 5). Higher EC values, regardless of the added amount of materials, were determined in the soil amended with PM and PL in the thermally unprocessed form. According to Solaiman and Anawar (2015), application of biochar to soil contributes significantly to a decrease in the content of salts easily soluble in a soil solution. This is connected with the sorption capacity of biochar, and this, in turn, arises from the process of production of the material (Nartey and Zhao, 2014). Moreover, the increase in soil EC values due to application of biochar was generally attributed to ash accretion as ash residues are generally dominated by carbonates of alkali and alkaline earth metals, variable amounts of silica, heavy metals, phosphates and small amounts of organic and inorganic N (Solaiman and Anawar 2015). Nigussie et al. (2012) also reported that the capacity of ashes to neutralize

Table 6. Content of Mn and Fe in mobile forms and organic matter-bound forms in soil.

Treatment	Fe mobile	Fe bound to organic matter	Mn mobile	Mn bound to organic matter
		mg kg^{-1}		
Soil	0.11 ± 0.03a	771 ± 49ab	13.79 ± 2.21d	47.3 ± 3.5a
Soil + PM 0.5%	0.90 ± 0.12cd	791 ± 23ab	10.99 ± 0.75c	51.0 ± 0.5a
Soil + PM 1%	0.15 ± 0.02a	789 ± 22ab	9.76 ± 0.89c	52.4 ± 0.7a
Soil + PM 2%	2.42 ± 0.02e	834 ± 27b	2.78 ± 0.44a	54.9 ± 2.5a
Soil + BPM 0.5%	0.32 ± 0.12ab	701 ± 55a	6.94 ± 0.38b	45.1 ± 5.5a
Soil + BPM 1%	0.29 ± 0.02ab	694 ± 45a	3.57 ± 0.36a	49.9 ± 7.4a
Soil + BPM 2%	0.76 ± 0.01bcd	704 ± 19a	1.24 ± 0.24a	50.3 ± 3.8a
Soil + PL 0.5%	1.14 ± 0.34d	772 ± 49ab	6.30 ± 0.29b	49.7 ± 3.9a
Soil + PL 1%	0.56 ± 0.28abc	784 ± 17ab	2.60 ± 0.20a	56.1 ± 7.8a
Soil + PL 2%	0.40 ± 0.16abc	742 ± 101ab	1.38 ± 0.12a	49.9 ± 7.0a
Soil + BPL 0.5%	0.75 ± 0.03bcd	724 ± 9ab	2.54 ± 0.33a	49.9 ± 5.1a
Soil + BPL 1%	0.76 ± 0.01bcd	682 ± 47a	1.24 ± 0.19a	52.0 ± 2.9a
Soil + BPL 2%	0.50 ± 0.19abc	733 ± 7ab	2.36 ± 0.18a	54.6 ± 0.2a

Each value represents the mean of three replicates ± standard deviation. The different letters within a column indicate a significant difference at p ≤ 0.05 according to Duncan's multiple range tests.
PM: Pig manure, PL: poultry litter, PMB: pig manure biochar, PLB: poultry litter biochar.

the acidic soil. In our presented research, application of PMB and PLB caused an increase in the value of EC in comparison with the soil from the control treatment, but to a lesser degree than application of unconverted PM and PL.

In general, the value of CEC was higher in treatments where organic materials had been applied than in the control. A greater increase in CEC, in comparison with the values of this parameter obtained after application of PM and PL, was observed after application of both biochars (PMB, PLB). The increase in the CEC value was also associated with the amount of added organic material. Numerous authors confirm the beneficial effect of biochar on the value of CEC of soils (Fellet et al., 2011; Yuan et al., 2011). As highlighted by Brodowski et al. (2005) and Cheng et al. (2006), an increase in soil CEC plays a substantial role in storage of water and of plant nutrients. This beneficial effect of biochar on the soil CEC should be attributed to physical features of biochar, mainly to the porous structure and specific surface area (Atkinson et al., 2010; Nartey and Zhao, 2014).

Content of Fe and Mn in mobile forms and in OM-bound forms

The effect of the used materials on mobility of Fe and Mn was examined after extraction of the most mobile forms of these elements with 1 M NH$_4$NO$_3$ solution (Table 6). The 2% amendment of PM and 1% amendment of PL caused an increase in content of Fe forms extracted with NH$_4$NO$_3$ in comparison with the content determined in soil from the control treatment. The 2% amendment of PMB caused an increase in the content of mobile forms of Fe, whereas in the case of amendment of PLB we recorded a decrease in mobility of this element.

The addition of organic materials to the soil caused a reduction in the content of mobile forms of Mn (Table 6). The amendment of PM to the soil contributed to a decrease in mobility of Mn from 20% to 80%, whereas the amendment of PL from 54% to 90%. Higher values of Mn immobilization were obtained with the larger addition of organic materials.

Application of PMB and PLB to the soil caused a similar immobilization of mobile forms of mobile forms of Mn.

Based on the sequential chemical extraction developed by Zeien and Brümmer (1989), the content of trace elements in fraction bound to soil OM was determined. It has been shown that the content of Fe and Mn extracted with 0.025 M C$_{10}$H$_{22}$N$_4$O$_8$ was higher than the content of these elements extracted with 1 M NH$_4$NO$_3$, mainly due to different extraction force of the solutions (Al-Wabel et al., 2015). The obtained results indicate that the amendment of organic materials to the soil did not have much effect on the content of Fe and Mn in the organic fraction (Table 6). When comparing the effect of PM and PL amendments with biochars produced from these materials (PMB, PLB), it was found that the content of Fe and Mn after application of unconverted and thermally converted materials was comparable.

The research results published so far indicate, that application of biochar to soil can cause liming effect as a result of decomposition of carbonates and hydroxides which are present in biochar. This, in consequence, may have a significant effect on the mobility of trace elements (Lucchini et al., 2014). In our research, we observed no directed changes in Fe mobility as well as a considerable decrease in Mn mobility. Undoubtedly, the considerable increase in soil pH as a result of application of organic materials (especially biochars) contributed to this. The obtained research results on the decrease in Mn mobility find confirmation in the results published by Al-Wabel et al. (2015). Reduction of acidification led to formation of poorly soluble Mn compounds in the soil. It should also be highlighted that the highly porous structure of biochar and the presence of functional groups did not have a significant impact on adsorption of Fe and Mn. According to Al-Wabel et al. (2015), amendment of biochar to soil has an effect on the content of available forms of both Fe and Mn. Fellet et al. (2011) also showed that biochar reduces the mobility of trace elements. Application of biochar may lead to changes of easily available forms of trace elements into forms which are chemically more stable, which in consequence causes a

reduction in their mobility and bioavailability (Ahmad et al., 2014a). According to Park et al. (2011), Usman et al. (2013), and Ahmad et al. (2014b), immobilization of trace elements in biochar-amended soil can be attributed to several chemical processes, including ion exchange, chemical sorption, and complexing on the surface. According to Park et al. (2011) and Usman et al. (2013), immobilization of trace elements in soil may take place as a result of precipitation with such mineral components as carbonates, silicates and phosphates. Choppala et al. (2012) reported that biochars can also limit the mobility of trace elements by altering the redox potential, exemplifying this in the effect of biochar amendment to soil on the changes of Cr^{+6} to Cr^{+3}. The relative participation of individual mechanisms in immobilization of trace elements after application of biochar remains unknown, although according to some authors like Houben et al. (2013), change in soil reaction (pH) is the main deciding factor.

CONCLUSIONS

The determined content of total forms of Mn and Fe in biochars was much higher compared to the content determined in the unconverted materials (pig manure [PM], poultry litter [PL]). As a result of thermal conversion of organic materials, PM and PL, a significant reduction in the content of Mn and Fe forms extracted with water was observed. The 2% amendment of PM biochar (PMB) caused an increase in the content of mobile forms of Fe, whereas in the case of the same dose of PL biochar (PLB) we recorded a decrease in mobility of this element. Application of PMB and PLB to the soil caused a similar immobilization of mobile forms of manganese as in the case of application of PM and PL that had not been thermally converted. The conducted research suggests that biochar can be a material that decreases bioavailability of trace elements which are potentially toxic for plants. It also indicates that biochar application to soil may have an effect on translocation and diffusion of trace elements (which depends on biochar porosity and presence of surface functional groups) in soil.

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