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HYGROSCOPIC MOISTURE CONTENT OF PODZOLIC SOIL WITH BIOCHAR

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Abstract. The main goal of this study was to investigate the effect of biochar on hygroscopic water content (maximum hygroscopicity) of grey-brown podzolic soil (Haplic Luvisol). The biochar was applied to the soil of sub-plots under fallow and grassland in the amount of 0 (control), 10, 20 and 30 Mg ha^{-1}. Soil samples were taken three times per year during the period of 2013-2015. Sorption isotherms of water vapour were determined for all studied samples and the maximum hygroscopicity (MH) was calculated from the relative water vapour pressure at p p_0^{-1} = 0.965. Value of the MH varied from 1.5 to 3%. The effect of biochar addition to soil on hygroscopic water content was ambiguous. Addition of biochar caused a slight decrease in MH value in the case of the grassland. For the fallow, a positive effect of biochar addition was observed.

Keywords: maximum hygroscopicity, biochar, grassland, fallow

INTRODUCTION

Biochar (defined simply as charcoal) is a carbon-rich product obtained from pyrolyzed biomass, during the heating under oxygen limited conditions (Lehmann and Joseph 2009, Jindo *et al*. 2014). Biochar amendments to agricultural soils have been shown to reduce nutrient leaching and to have positive effects on soil physical, chemical and microbiological properties (Aslam *et al*. 2014, Sun and Lu 2014, Ścisłowska *et al*. 2015, Gul *et al*. 2015, Xie *et al*. 2015). Several researches showed that the properties of biochars are related to the type of source material, production method and conditions (Yargicoglu *et al*. 2015, Jindo *et al*. 2014, Zhao *et al*. 2013).

Water in soils exists as hygroscopic (bounded water), capillary and free water. Hygroscopic water content is an extremely thin water layer surrounding soil mineral surfaces and is greatly affected by the relative humidity (Amer 2009, Amer 2015, Matiushkina and Kharitonova 2015). Hygroscopic moisture content of soil is usually determined by an air drying method and has been related with the clay content, the surface area and cation exchange capacity of the soil (Shah and Singh 2006, Tarrent *et al*. 2015, Leăo *et al*. 2014, Moiseev 2008, Verstraeten *et al*. 1971, Matiushkina and Kharitonova 2015, Parakash *et al*. 2014). The adsorption isotherms belong to basic hydrophysical characteristics describing the relationship between the relative humidity or the relative water vapour pressure and the equilibrium water content in soil. Water sorption isotherms are equivalent to the water retention curves that display the soil water content as a function of the logarithm of water potential. The water potential is a measure of water activity in the soil and is directly related to the relative humidity in the surrounding air. The above relationship is given by the Kelvin equation (Amer 2015, Schneider and Goss 2012). One of the parameters which can be estimated from the adsorption isotherm of water vapour is the maximum hygroscopicity (MH) or hygroscopic coefficient (Chong Chen *et al*. 2013). The maximum hygroscopicity is expressed as the amount of adsorbed water at the relative pressure, $p\ p_0^{-1} \approx 0.9645$. The term hygroscopic coefficient characterises only the hygroscopic properties of soils (Kutilek and Nielsen 1994).

Walczak *et al*. (2002) presented the static and dynamic hydrophysical characteristics of Polish arable soils. In all studied profiles they found that the variability and differentiation in the amount of water not easily available for plants was much larger than the amount of easily available water. The content of water not easily available for plants in the surface layer varied from 4.4 to 19.8%. vol., in subsurface layer – from 2 to 17.1% vol. and in the subsoil –from 0.3 to 19.9% vol. The maximum quantity of this kind of water was retained in soils derived from loess and clays, Chernozems and Fluvisols. It is very important that Polish soils retain a very small quantity of water available for plants – only less than 9% vol.

The main goal of this study was to investigate the influence of biochar addition on the state of the soil maximum hygroscopicity. Our work was focused on the observation of changes, during a few years, in Haplic Luvisol soil used as a grassland and as fallow. To this end, sorption isotherms of water vapour were determined to calculate the maximum hygroscopicity of studied samples with biochar addition.

MATERIALS AND METHODS

The experimental plots are located in Felin, near the city of Lublin (51°15′N, 22°35′E). The studies were conducted on a Haplic Luvisol (according to the IUSS Working Group WRB., 2006) derived from loess with a clay, silt and sand content, for the 0-20 cm soil layer, of 7, 29, and 64%, respectively. The soil acidity measured in H_2O reached 5.9 of pH unit, and the organic matter content was 1.15%.

The fallow surface had been left unseeded after being tilled (to a depth of 20 cm) and harrowed for 10 years prior to the experiment. During the experiment the fallow plots were maintained without plants. The grassland was established at least 35 years ago and managed through cutting. In the grassland and fallow fields of 20 m^2 (4×5 m), dry biochar was uniformly surface applied in sub-plots at the amount of 0 (grass control and fallow control), 10 (grass1bioC and fallow1bioC), 20 (grass2bioC and fallow2bioC) and 30 (grass3bioC and fallow3bioC) Mg ha^{-1} in May/June 2013. Then it was mixed to a depth of 0-15 cm in the case of the fallow, using a rototiller, and it was left on the surface in the case of the grassland. The micro plot experiment is described in detail by Usowicz *et al*. (2016). The soil samples (three soil sample from each sub-plot) were taken from the fallow and grassland three times per year during the period of 2013-2015, i.e. in March, July and November (description of the samples collected in given year: I, II and III). The monthly weather conditions during the experiment are collected in Table 1.

Table 1. Average monthly weather conditions during the experiment (http://en.tutiempo.net /climate /poland.html)

Date	Name of soil sample	Temperature (°C)	Humidity (%)	Rainfall (mm)
July 2013	2013-II	18.6	74.1	88.14
November 2013	2013-III	5.20	90.6	74.92
March 2014	2014-I	6.00	73.7	47.76
July 2014	2014-II	20.2	73.1	87.37
November 2014	2014-III	4.20	89.9	22.85
March 2015	2015-I	4.70	73.7	39.11
July 2015	2015-II	19.3	65.9	47.50
November 2015	2015-III	4.70	87.3	41.39

The biochar used in the experiment is a commercial product – Biochar FLUID made by FLUID S.A. company (Poland). Product physicochemical characterisation includes: 77% of carbon, 18% of volatile matter, 5% of ash and < 0.01% of sulphur, chlorine and other, nitrogen ~0.4%, pH ~ 8.0, bulk density ~ 0.33 Mg m^{-3}, and particle density 1.41 Mg m^{-3} (http://fluid.pl/en/offer/production-and-sales-of-biocarbon-fluid-brand-for-the-power-industry-and-agriculture/).

The adsorption-desorption isotherms of water vapour were performed by gravimetric method and the specific surface area was obtained in agreement with the Polish standard method (PN-Z-19019-1, 1997). Before the adsorption measurement the soil samples were dried in a vacuum chamber with concentrated sulphuric acid until the sample weight reached constant values. Soil samples with weight equal approximately to 3g were put into a glass vessel and placed over sulphuric acid solution. Then they were equilibrated with water vapour during two days. The amount of adsorbed water vapour was computed as the difference between the weight of the sample with water and the dry sample (dried in an oven at 105°C). The relative water pressures were obtained from the density of sulphuric acid solutions. Twenty levels of relative pressure were selected in the range of 0.015 to 0.95. The variation in replicated data did not exceed ±5% at the lowest vapour pressure and ±1% at the highest vapour pressure. The adsorption measurements were replicated three times, keeping the temperature constant, T = 20°C ±0.5. The averaged values were used to obtain the maximum hygroscopicity and to prepare the Figures. Maximum hygroscopicity (MH in %) was estimated from sorption isotherms at the relative water vapour pressure $p\ p_0^{-1} = 0.965$ and expressed as the amount of the sorbed water vapour ($g\ g^{-1}$) multiplied per 100.

RESULTS AND DISCUSSION

Figure 1 shows an example of experimental adsorption isotherms obtained for soil samples from the fallow and grassland which were collected in July 2013. According to the BET classification (Gregg and Sing 1978), all the curves belong to the same class, namely to the type II. Type II isotherms (S-shaped or sigmoid) are monolayer-multilayer isotherms which are normally obtained with non-porous or macroporous materials. These curves are characterised by the sharpness of the knee of the isotherm. The rounded knee of the isotherms suggests low net heat of adsorption and low adsorbent-water vapour interaction.

In general, the shape of the adsorption curves is similar and suggests low soil-water interaction (Fig. 1). However, the detailed course of the curves illustrates that the amount of adsorbed water varies between investigated soil samples and this observation is connected with the addition of the biochar and the way of the land use. It is well known that soil water retention is largely a function of texture and organic matter content, determining the amount of fine pores and surface area on which adsorption take place (Poeplau *et al*. 2015). The water uptake by biochars is dependent on both feedstock selection, which controls residual macroporosity, and production temperature, which controls hydrophobicity and pyrogenic nanopore formation (Gray *et al*. 2014).

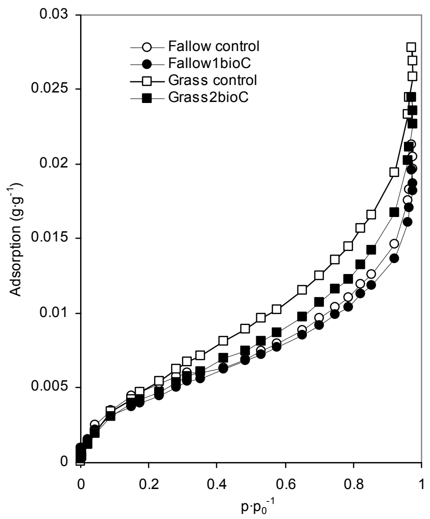

Fig. 1. Selected water vapour adsorption isotherms for soil samples collected from fallow and grassland in July 2013

The adsorption data have been used to evaluate the values of the maximum hygroscopicity (MH) of the investigated samples. The results are shown in Fig. 2a for soil samples taken from the fallow and in Fig. 2b for samples from the grassland.

The value of the maximum hygroscopicity (MH) varied from 1.5 to 3.3% for all soil samples (Fig. 2a and Fig. 2b). These findings are in agreement with results obtained by Król (1963) for soil from middle climatic zone of Poland, and Trzecki (1976) who found a correlation between the content of clay particles and the moisture of permanent wilting of plants and the maximal higroscopicity in arable soils. Our study showed that soil material originated from the grassland exhibited higher values of MH (about 2~3.3%) than the soil samples from the fallow (about 1.5~2.5%). These differences were especially clearly visible for the control soils for which MH is higher than 3% in the case of the grassland. Podstawka-Chmielewska and Kurus (2011) estimated the direct and the after effect of various methods of arable land fallowing on the moisture and bulk density of soil. They observed the least moisture under green fallows and the biggest soil moisture decrease in half of the vegetation period, especially on fallow fields with cover crops. Bryś (2008) pointed out the buffering role of vegetation in soil temperature on grassy field and bare soil. Also Pranagal *et al.* (2007) found that after ten years in a fallow state the physical condition of Haplic Podzol improved; a decrease in soil compaction and an increase in field water capacity can be regarded as especially valuable.

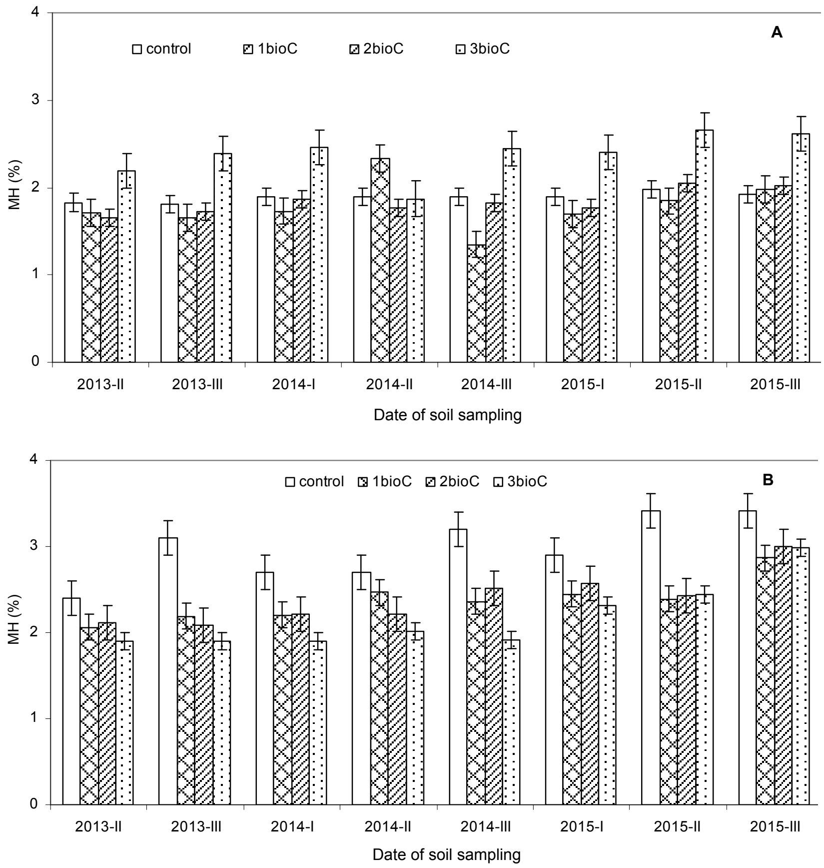

Fig. 2. Maximum hygroscopicity (MH) of investigated soil samples from fallow (A) and grassland (B) taken in period of 2013-2015, i.e. in March (I), July (II) and November (III); average values from 6 replicates in 2013 and 9 replicates in 2014-2015, ± – standard deviation

The effect of biochar addition to soil on MH is ambiguous. In the case of grassland the addition of biochar caused a decrease in MH value with increasing biochar dose in the years 2013-2014, and an increase in 2015 (Fig. 2b). For the fallow, the increase of MH with the dose of biochar takes place and is more visible for the soil samples with the maximum dose of the biochar (Fig. 2a). The linear determination coefficients between MH and biochar dose were 0.461 and 0.315 for soil samples from fallow and grassland, respectively. Improved water retention in varied magnitude is commonly reported in biochar amended soils (i.e.

Abel *et al*. 2013, Castellini *et al*. 2015). Ajayi and Horn (2016) investigated two soils with distinct texture with equivalent rates of slowly pyrolysed biochar and found that the available water capacity was significantly higher in the amended substrates, particularly in amended fine sand. The addition of biochar increased the saturated hydraulic conductivity of the silty substrates while it was decreased in the sandy substrates. Usowicz *et al*. (2016) reported changes in soil thermal properties in response to biochar application – the average thermal conductivity and water content were greater under grass than fallow.

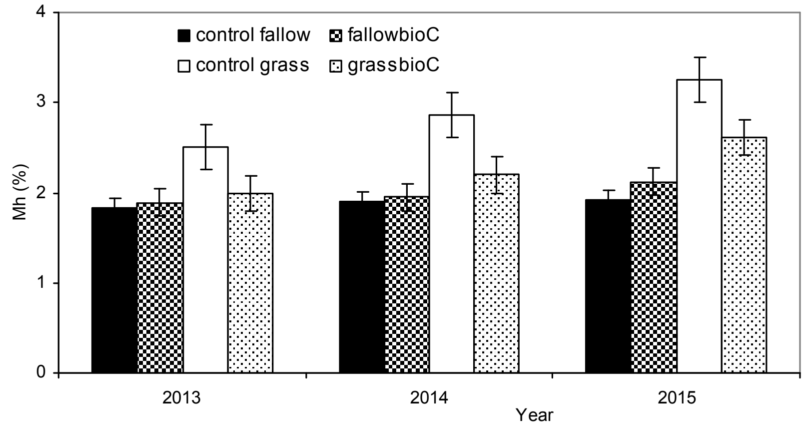

Fig. 3. Annual average value of MH for control soil samples (A) and soil samples with biochar; average value from 3 replicates in 2013 and 6 replicates in 2014-2015, ± – standard deviation

Fig. 3 shows the average values of MH for grassland and fallow in the years 2013-2015. It should be noted that the results for control soil samples were treated summarily as one data collection and those for soil samples with different doses of biochar also as one data collection. The annual (in the period of 2013-2014) MH values of the soil practically did not change for the variants of fallow and grassland, however, a slight increase of MH value of soil samples with biochar was observed. This increase is more visible for grassland in 2015. We found the linear relationship between the annual value of MH and biochar dose, for which the determination coefficient varied from 0.783 to 0.824 and from 0.788 to 0.846 for fallow and grassland, respectively.

The weather conditions during the experiment (Table 1) had a weak effect on MH values of the investigated soil samples from fallow and grassland. The determination coefficient between MH and temperature or rainfall varied from 0.011 to 0.182. Only between humidity and MH the coefficient was 0.261 (grassland) and 0.595 (fallow).

It is known that soil organic matter is one of the important factor determining surface properties of soils and sorption of water vapour (Esmaeilzadeh and Ahangar 2014, Murphy 2015). Different kinds of functional groups were identified in soil organic matter and in mineral soil components (Boguta and Sokołowska 2014). Several polar functional groups serve as sorption sites for water molecules. These groups create primarily hydrogen bonding or van der Waals forces or π-bonding. Because of a high dipole moment and ability to form hydrogen bounds, water is adsorbed in a highly specific manner, forming quite a complex adsorbed layer.

The effect of added biochar on soil properties is probably connected with its physical and chemical properties. Yargicoglu *et al*. (2015) determined the hydraulic conductivity and water holding capacity for six biochars produced commercially using waste wood. They found that the water holding capacity varied from 32.9 to 63.9% on a wet weight basis or in the range of 50.6-179.4% on a dry weight basis. They found also that the finer-grained biochars generally had higher value of water holding capacity. The presence of micropores in biochars made it also highly preferable for gas adsorption. The structure of biochars is connected with the pyrolysis temperature, and the total water uptake of biochar media depends on capillary forces as well as porosity (Gray *et al*. 2014). Increase in temperature led to the formation of biochars with an aromatic carbon structure and more stable forms of carbon. The oxygen-containing functional groups on the biochar surfaces determined the acid/base properties of the material. The molar O/C ratio of a char practically indicates its surface hydrophilicity (Chun *et al*. 2004). The hydrophobicity of biochars decreased with increasing production temperature and could have been be due to aliphatic functionality which is volatilised and lost at higher production temperatures (Gray *et al*. 2014). The polar groups on activated carbon and biochar surfaces act as water adsorption centres and facilitate the formation of water clusters on the surfaces. An increase in porosity and surface area of biochars with increasing treatment temperatures and activation is reported (Keiluweit *et al*. 2010, Gray *et al* 2014, Lei and Zhang 2013). Ajayi and Horn (2016) report results that provide more detailed insights into the effect of biochar addition on water properties of soil. The biochar material is hydrophobic (index R = 2.23) while the sandy loamy silt and fine sand are hydrophilic (index R = 1.73 and 1.17 respectively). Amending both soils with biochar 20 g kg^{-1} increased the index R. The index R was slightly decreased with 50 g kg^{-1} amendment rate, but increased again with 100 g kg^{-1} amendment rate.

Generally, the effect of biochar addition on water properties of soil depends of the biochar and soil properties. The structure of biochars is connected with the pyrolysis temperature and the total water uptake of biochar media depends on capillary forces as well as porosity. The polar functional group on biochar surface may act as water adsorption centres and facilitate the formation of water clusters on the surfaces. Also the presence of micropores in biochars makes them highly preferable for gas adsorption. The effect of biochar in agricultural soils depends also on the texture of the soil and on the amount of added biochar. The amendment rate of biochar increased or decreased the hydrophlic/hydrophobic index of soil.

CONCLUSIONS

1. The maximum hygroscopicity (MH) for all soil samples taken three times per year during the period of 2013-2015 varied from 1.5 to 3.3%. Soil samples from grassland exhibited higher values of MH (about 2 ~ 3.3%) than soil samples from fallow (about 1.5 ~ 2.5%).

2. The effect of biochar addition to soil on MH was ambiguous. In the case of the grassland, the addition of biochar caused a decrease of MH value with increase of biochar dose in the years 2013-2014 and an increase in 2015. For the fallow the increase of MH with the dose of biochar took place and it was more visible for the soil samples with the maximum dose of the biochar.

3. The annual (in the period of 2014-2015) MH values of the soil did not change in both variants of our experiment. However, a slight increase in MH was observed in the case of soil samples with biochar addition. Moreover, a linear correlation was found between the annual value of MH and biochar dose.

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ZAWARTOŚĆ WODY HIGROSKOPOWEJ W GLEBIE PŁOWEJ Z BIOWĘGLEM

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Streszczenie. Głównym celem pracy było zbadanie wpływu biowęgla na maksymalną higroskopijność gleby płowej. Biowęgiel dodawano na poletka ugorowane i obsiane trawą w ilości 0 (kontrola), 10, 20 i 30 $Mg{\cdot}ha^{-1}$. Próbki gleby pobierano trzykrotnie w ciągu roku w latach 2013-2015. Izotermy sorpcji pary wodnej zostały wyznaczone dla wszystkich badanych próbek, a maksymalną higroskopijność (MH) obliczono przy względnym ciśnieniu pary wodnej $p{\cdot}p_0^{-1}$ = 0,965. Wartość MH wahała się w zakresie 1,5-3,3%. Wpływ dodatku biowęgla na maksymalną higroskopijność był niejednoznaczny. Dodatek biowęgla spowodował nieznaczny spadek MH w przypadku poletek obsianych trawą i wzrost w przypadku ugoru.

Słowa kluczowe: maksymalna higroskopijność, biowęgiel, użytki zielone, ugór