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Physical Properties of Soil-Biochar Mixtures - a Laboratory Study

Diploma Thesis

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Declaration

I hereby declare that this Master's Thesis titled "*Physical Properties of Soil-Biochar Mixtures - a Laboratory Study*" is my own work with the expert guidance of my thesis supervisor and my consultant and all the sources have been cited and acknowledged by means of complete references. As an author of the thesis I declare that, in association with writing it, I did not infringe copyrights of third persons.

Prague, April 10 2016

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Hailemeleket Teklu Kidane

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**PHYSICAL PROPERTIES OF SOIL-BIOCHAR
MIXTURES - A LABORATORY STUDY**

Abstract

Physical Properties of Soil-Biochar Mixtures - a Laboratory Study

Recently, biochar's potential use in soil management and amendment has gained a considerable interest globally. Growing evidence demonstrated that biochar results in sustainable property management when it is applied to the soil. However, biochar vary considerably in terms of physical and chemical properties and its benefits. Previous studies on biochar have been mainly focused on the chemical and nutritional effects. Little is known about the effect of biochar on the physical properties of soils. Therefore, the objective of this thesis was to determine the influence of biochar on the physical and hydrophysical properties of some soils from the Czech Republic.

Three model soil types were investigated used such as; a standard fine silica sand (SA), the Suchdol silty loam Chernozem (CH), and a light Cambisol (CM). The biochar concentration treatments were a control without admixture of biochar (B0); a treatment with addition of 0.001 g/g (B1) and a treatment with addition of 0.01 g/g (B2). Each treatment was carried out in triplication.

The data collected were soil porosity, bulk density and particle density measured by standard methods (drying, weighing, pycnometer). Then the saturated and unsaturated hydraulic conductivity, wettability and retention curve (up to the suction about 80 kPa) were measured with Decagon Minidisk tension infiltrometer and UMS Hyprop evaporation equipment. The experiments were carried out in the Department of Water Resources laboratory.

Altogether, we can say that the effect of biochar addition on the soil physical properties is clearly perceivable but not as strong as one might expect. The identified effects of biochar addition are the decrease in sorptivity, the increase in saturated hydraulic conductivity and the increase in the water retention capacity. However, these effects are not obvious and are not always observed. This would probably happen with the higher doses of biochar above the economic limits.

Keywords: Carbonisation, water retention, hydraulic conductivity, infiltration, water repellency

Abbreviations and Acronyms

AWC, Available water capacity;

C, Carbon

CaO, Calcium oxide

CEC, Cation exchange capacity

CH, Chernozem Soil

CH₄, Methane

CM, Cambisol Soil

CO, Carbon monoxide

CO₂, Carbon dioxide

FC, Field capacity

Fe₂O₃, Iron (III) oxide

H₂, Hydrogen

IBI, International Biochar Initiative

K₂O, Potassium oxide

K_{sat} = Saturated hydraulic conductivity

MgO, Magnesium oxide

N, Nitrogen

Na₂O, Sodium oxide

NRCS USDA, Natural Resources Conservation Service, United States Department of Agriculture

PAWC, Plant available water holding capacity

PWP, Permanent wilting point

RETC, Retention Curve software computer program for fitting measured data to different models developed for soil water retention curve

SA, fine silica sand (ST 56)

SiO₂, Silicon dioxide

SWRC, Soil Water Retention Curve

SWR, Soil water repellency

WHC, Water holding capacity

WRB, World reference base

Table of Contents

Declaration.....	i
Acknowledgements.....	ii
Abstract.....	iv
Abbreviations and Acronyms	v
Table of Contents.....	vi
List of Tables	viii
List of Figures.....	ix
1. Introduction.....	1
2. Scientific Hypothesis and Objectives	4
2.1. Objective	4
2.2. Hypothesis.....	4
3. Literature Review	5
3.1. Pyrolysis and biochar	5
3.2. Interest for biochar in environmental applications.....	8
3.3. Physical properties of biochar	11
3.4. Effect of biochar on soil physical and hydrophysical properties	13
3.4.1. Soil water retention.....	15
3.4.2 Hydraulic conductivity	18
3.4.3 Water repellency (hydrophobicity)	19
4. Materials and Methods.....	21
4.1. Location.....	21
4.2. Soils.....	21
4.3. Treatments.....	24
4.4. Sample preparation.....	24
5. Results.....	38

5.1. Sorptivity..... 38

5.2. Saturated hydraulic conductivity..... 43

5.3. Soil water retention curves..... 45

6. Discussion..... 47

6.1. Sorptivity..... 47

6.2. Saturated hydraulic conductivity..... 48

6.3. Soil water retention curves..... 48

7. Conclusions..... 50

References..... 51

Appendices..... 64

List of Tables

Table 1. Characteristics of Terra Preta soils under various land use types (i.e., secondary forest, grassland and agricultural land), compared to nearby unamended Oxisols (Gul et al., 2015)	10
Table 2. Characteristics of the three soils (CH, CM and SA) and the biochar used for this study.	22
Table 3. Chemical analysis of the fine silica sand, ST 56, with Roentgen - fluorescent analysis (RFA) (Sklopísek Střeleč, a.s., 2015)	23
Table 4. Van Genuchten parameters for 12 soil texture classes and values of A for the Minidisk Infiltrometer with suction values from 0.5 to 7 cm (Decagon Devices, Inc., 2016).	28
Table 5. Experimental setup for MPS-2 sensors soil water retention measurement.	36
Table 6. Basic results of the Minidisk infiltration measurements	39
Table 7. Average saturated hydraulic conductivity of the overall measurements	43
Table 8. Average water contents of silica sand at typical matric heads h (cm).....	45

List of Figures

Figure 1. Thermochemical decomposition of various organic materials into a C-rich solid, bio-oil and a non-condensable gas product through pyrolysis process (modified from Brownsort, 2009).	6
Figure 2. The concept of biochar production system by low-temperature pyrolysis in conjunction with biochar sequestration when applied to the soil. Typically, about 50 % of the pyrolyzed biomass is converted into biochar (Lehmann, 2007a).	7
Figure 3. Soil profile and productivity of Terra Preta soils (<i>darker soil in the right side</i>) compared to nearby unamended Oxisols (IBI, 2016).	9
Figure 4. Scanning Electron Micrographs of (A): chicken litter 250 °C biochar; (B): chicken litter 250 °C steam activated biochar; (C): chicken litter 480 °C biochar; (D): chicken litter 480 °C steam activated biochar; (E): wood chip 250 °C biochar; (F): wood chip 250 °C steam activated biochar; (G): wood chip acid activated biochar; (H): wood chip 500 °C biochars; (I): wood chip 500 °C steam activated biochars; and (J): wood chip 500 °C acid activated biochar (Lima et al., 2015).	12
Figure 5. KSAT device (KSAT operation manual; UMS GmbH., 2013).	31
Figure 6. Immersion method of saturating the soil core samples (KSAT operation manual; UMS GmbH., 2013).	32
Figure 7. HYPROP device. The position of the microtensiometers at the HYPROP unit (HYPROP operation manual; UMS GmbH., 2010).	34
Figure 8. Average values of the coefficient C_2 (a proxy to sorptivity) – all data	38
Figure 9. Average values of the coefficient C_2 (a proxy to sorptivity) – water infiltration	40
Figure 10. Average values of the coefficient C_2 (a proxy to sorptivity) – ethanol infiltration	40
Figure 11. Average values of the coefficient C_2 (a proxy to sorptivity) – Cambisol	41
Figure 12. Average values of the coefficient C_2 (a proxy to sorptivity) – Chernozem	41

Figure 13. Average values of the coefficient C_2 (a proxy to sorptivity) – Silica sand 42

Figure 14. Averages of repeated hydraulic conductivity measurements of individual samples (replications) 44

Figure 15. Average hydraulic conductivities over all replications 44

Figure 16. Comparison of water retention carried out on sand with different concentration of biochar – the whole range measured with HYPROP and MPS-2, with a logarithmic vertical scale, $pF = \log_{10}(h(\text{cm}))$ 45

Figure 17. Comparison of water retention carried out on sand with different concentration of biochar – the moist range, measured mainly with HYPROP and only marginally by MPS-2, with a linear vertical scale. 46

1. Introduction

Biochar is the charcoal produced by chemical decomposition of various organic materials through pyrolysis in the nonattendance or with limited access of oxygen (Bridgwater and Peacocke, 2002; Demirbas and Arin, 2002). It was viewed early as an energy source and likewise utilized for water purification, gas cleaning, metallurgical industries and for charcoal in home cooking. Presently, biochar has gained considerable global interest and promotion for its potential use in soil management and amendment (Lehmann et al., 2006; Shackley et al., 2013).

Scientific evidences carried during recent years demonstrates that biochar has the potential to deliver a variety of sustainability outcomes such as carbon dioxide (CO₂) and other greenhouse gases sequestration with opportunities for C trading (Pessenda et al., 2001; Lehmann, 2007b). It reduces the environmental burden posed by animal and crop wastes, especially their polluting ground and surface waters (Carpenter et al., 1998; Dias et al., 2007; Matteson and Jenkins, 2007), in addition to reducing their volume and weight (Ackerman, 2000; Cantrell et al., 2007). Energy is released during the biochar production processes (Bridgwater et al., 1999; Bridgwater, 2003). Biochar is free from potential pathogens that may pose challenges to direct soil application of animal manures (Bicudo and Goyal, 2003) or sewage sludge (Westrell et al., 2004). It increases the cation, anion and pollutant sorption capacity and pH of the soil (Liang et al., 2006; Cheng et al., 2008), creating hydrophobic sites (Rumpel et al., 2006) and increasing adsorption sites for microbes (Baldock and Smernik, 2002; Hamer et al., 2004; Hockaday et al., 2006, 2007), minerals (Brodowski et al., 2005) or pesticides (Smernik et al., 2006). Thereby it improves nutrient retention and nutrient availability, reduces leaching of nutrients and other contaminants. It potentially increases water availability to plants, improves mycorrhizal activity (Warnock et al., 2007) and provides benefits to other groups of microorganisms and their functions in the soil. It improves soil structure and soil aeration (Kolb, 2007). Crop productivity improvement was also observed with the addition of biochar (Lehmann and Rondon, 2006; Jeffery et al., 2011). Furthermore, biochar is a more stable solid than the common organic conditioners, due to its very low degradation rate.

Thus, its potential effects on the chemical, physical and biological properties of the soil may continue over a long period of time (Atkinson et al., 2010).

The above effects come from the chemical and physical properties of the biochar and its interaction with the soil. Many studies on biochar are focused mainly on the chemical and nutritional effects. There are less published results on the effect of biochar on the physical properties of soils (Atkinson et al., 2010). The latter effect is due to biochar's highly porous structure, large specific surface and the ways in which the biochar is packed together with soil particles and aggregates (Downie et al., 2009; Major et al. 2009; Atkinson et al. 2010; Sohi et al., 2010; Verheijen et al., 2010). When biochar is applied to the soil, it influences its total specific surface, texture, structure, porosity and consistency through changing the pore-size distribution, particle-size distribution, packing of soil particles and the bulk and particle density of the soil. These changes in the soil physical characteristics directly affect the soil's response to water, its aggregation, workability during soil preparation, swelling-shrinking dynamics and permeability, as well as its capacity to retain cations, anions and pollutants and its response to ambient temperature changes (Chang et al., 2007; Brady and Weil, 2008). By this, it influences all of the essential functions of the soil like fertility, including water, air, nutrient cycling and microbial activity (Troeh and Thompson, 2005). Biochar's effect on soil physical properties probably has a direct influence on crop productivity (Cornelissen et al., 2013).

However, there is a considerable variation in the physical and chemical properties of various types of biochar. Hence, the benefits vary, too. The biochar properties depend on the starting organic material (feedstock) and the production conditions, including the pyrolysis temperature and duration and the pre- and post-treatment processes. The biochar influence on the soil depends, in particular, on the amount used and the soil type (Darmstadt et al., 2000; Brown et al., 2006; Lehmann and Rondon, 2006; Lehmann, 2007b; Peake et al., 2014). Moreover, the economic effectiveness of applying biochar for soil management is uncertain. The spatial and temporal availability of suitable feedstock, its cost, the cost of production, transportation and application of the biochar and other conditions must be taken into account. In addition, due to the assumed stability and long half-life of biochar, its effects on the properties of soils is hard to quantify in a

short-term study. Thus, biochar deserves further comprehensive studies to elucidate its characteristics and benefits for sustainable soil amelioration and soil management.

2. Scientific Hypothesis and Objectives

2.1. Objective

To investigate how the soil physical and hydrophysical properties of three typical soils are affected by various admixtures of biochar.

2.2. Hypothesis

The admixtures of biochar augment soil water storage capacity, especially in light soils, increase soil's infiltration capacity, hydraulic conductivity (both saturated and unsaturated), internal drainage and aeration of the topsoil, especially in medium and heavy soils, and reduce the wettability of the soil.

3. Literature Review

3.1. Pyrolysis and biochar

Pyrolysis is a thermochemical decomposition of various organic materials into a C-rich solid, bio-oil and a non-condensable gas product in the nonattendance or with limited access of oxygen at relatively low temperatures ($<700\text{ }^{\circ}\text{C}$) (Zanzi, 2001; Bridgwater and Peacocke, 2002; Demirbas and Arin, 2002; Brownsort, 2009). This process of decomposition converts the biomass into three products: 1. a non-condensable gas product also known as ‘syngas’ or ‘pyrolysis gas’ containing carbon monoxide (CO), carbon dioxide (CO₂), hydrogen (H₂), methane (CH₄) and higher hydrocarbons; 2. A bio-oil, which is a liquid product also known as pyrolysis oil or bio-crude; 3. a solid charcoal or char with high content of carbon, which have various uses; it is also termed as biochar, or coke (Figs. 1 and 2) (Brownsort, 2009).

The thermochemical conversion processes generates renewable fuels such as combustible gas (syngas) and bio-oil, and biochar is left as a byproduct. The most common types of thermochemical conversion are slow and fast pyrolysis, gasification and hydrothermal carbonization. As the cost and scale of production are commercially feasible, the slow and fast pyrolysis pathways are often employed to make biochar, which could be used as a soil amendment for agriculture. Essentially, slow pyrolysis biochar is a product of traditional heating of feedstocks under oxygen-limiting conditions, which helps for cooking and house-warming purposes. It is obtained by heating the feedstocks at temperatures from 300 to 800 °C at atmospheric pressure for hours to days (Brewer and Brown, 2012). The fast pyrolysis aims at maximizing the production of bio-oil by rapid quenching of vapor produced from burning biomass at higher temperatures (400–1000 °C) with fast heating rates, typically higher than 300 °C s⁻¹ for few hours (i.e., 1–2 h) (Brewer and Brown, 2012; Mohanty et al., 2013).

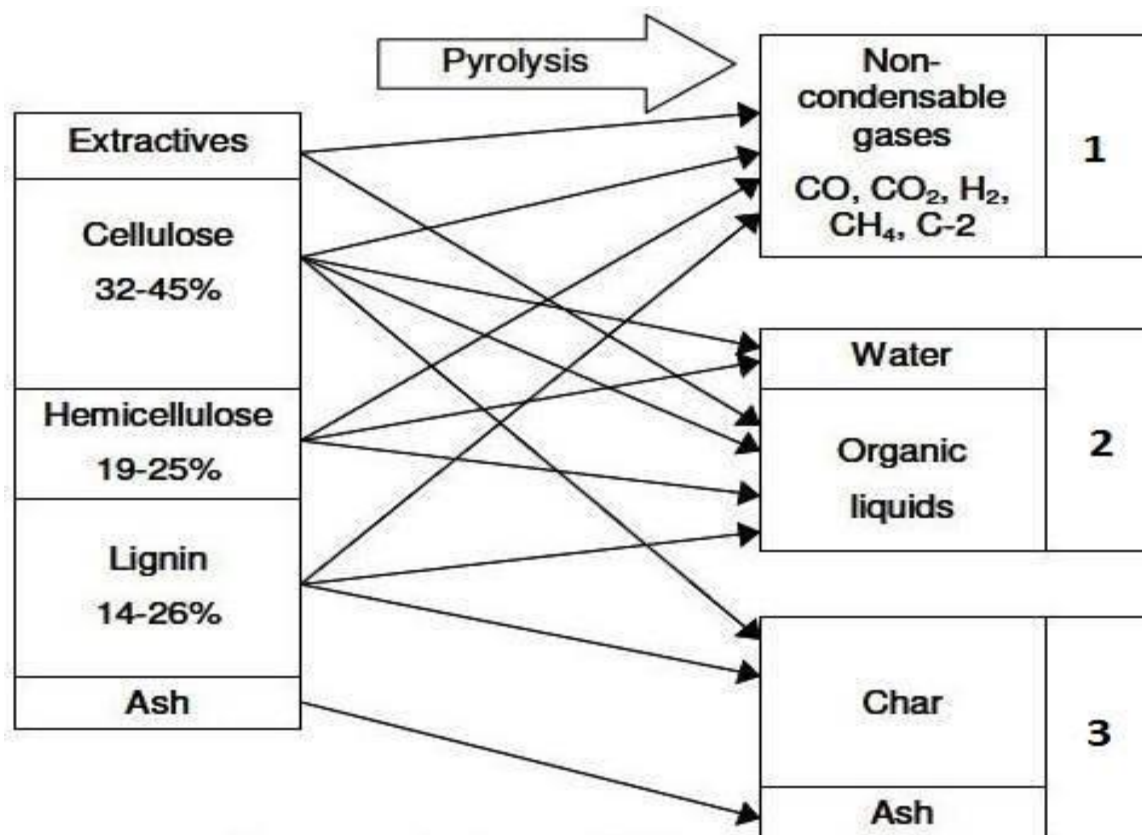


Figure 1. Thermochemical decomposition of various organic materials into a C-rich solid, bio-oil and a non-condensable gas product through pyrolysis process (modified from Brownsort, 2009).

Biochar is a carbon-rich material produced by the slow thermochemical pyrolysis of biomass materials such as livestock manures, sewage sludge, crop residues and composts. It has a highly heterogeneous composition and its condensed aromatic nature makes it relatively stable in the environment. Biochar has a recalcitrant carbonaceous component (Glaser et al., 2002) that may possess a microporous as well as reactive surface (Brennan et al., 2001). The biochar structure is essentially amorphous, but may locally contain crystalline structures highly ordered graphene sheets. The total carbon content of biochar varies considerably depending on feedstock and may range from 400 g kg⁻¹ up to 900 g kg⁻¹. One of the typical biochar production systems is shown in Fig. 2 (Lehmann, 2007a).

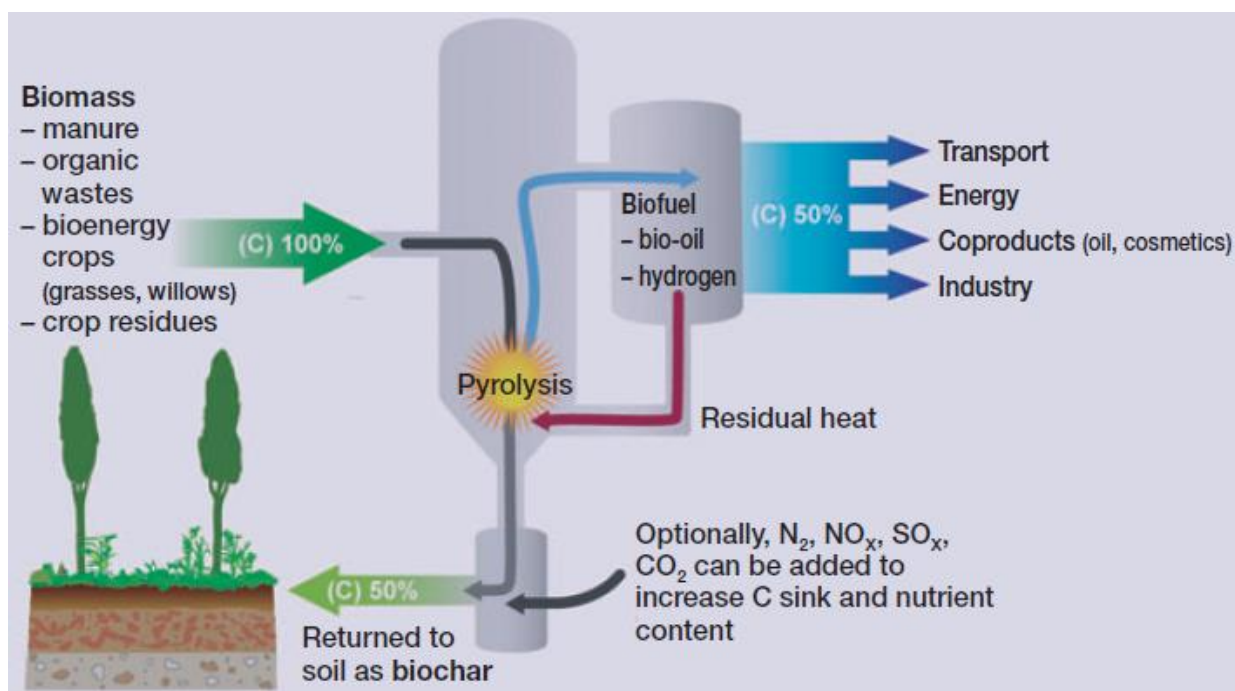


Figure 2. The concept of biochar production system by low-temperature pyrolysis in conjunction with biochar sequestration when applied to the soil. Typically, about 50 % of the pyrolyzed biomass is converted into biochar (Lehmann, 2007a).

The physico-chemical characteristics of slow- and fast-pyrolysis biochars depend on the feedstocks and production temperature used. Higher production temperatures yield biochars with greater surface area and porosity (Mukherjee et al., 2011; Brewer and Brown, 2012; Mohanty et al., 2013), more alkaline pH, higher carbon to nitrogen (C:N) ratio (Singh and Cowie, 2010; Cantrell et al., 2012; Novak et al., 2013; Ronsse et al., 2013) and lower dissolved organic carbon concentrations (Uchimiya et al., 2013; Budai et al., 2014; Rajapaksha et al., 2014). These variations in biochar characteristics have implications when biochar is applied as a soil amendment. Depending on the native soil properties (e.g., texture and organic matter content), biochar inputs can cause negligible to significant alteration of soil physico-chemical and biological properties.

The chemical composition of the biomass feedstock has a direct impact upon the physical nature of the biochar produced. At temperatures above 120 °C, organic materials begin to undergo some

thermal decomposition, losing chemically bound moisture. Hemicelluloses are degraded at 200°C to 260 °C, cellulose at 240 °C to 350 °C, and lignin at 280 °C to 500 °C (Fig. 1) (Sjöström, 1993).

3.2. Interest for biochar in environmental applications

Biochar has recently garnered interest for agricultural and environmental applications owing to its unique physicochemical properties, though it was used as a soil amendment for at least 2000 years in the Amazon basin of Brazil, where the soils affected by it are now called “Terra Preta”. Finely divided biochar remained in soils in humid tropical climates, such as the Amazon, for thousands of years (Sombroek et al., 2003), resisting the rapid rates of mineralization common to organic matter in these environments and producing a distinct black color (Fig. 3). Such biochar is typically older than any other form of carbon in soils (Pessenda et al., 2001). The discovery of this anthropic soil sparked the recent considerable interest in the usage of biochar as a carbon sequestration agent and as a soil amendment for improved agricultural productivity (Lehmann et al., 2006; Shackley et al., 2013). Terra Preta, which is translated as “dark earth” and often labeled as Amazonian Dark Earths, has been found in the Amazon and associated with increased soil productivity in otherwise highly unproductive tropic oxisols (Lehmann and Rondon, 2006). Its high contents of aromatic black carbon and organic matter are attributed to anthropogenic enhancement of the soil, since there were no other reported differences between Terra Preta and nearby soils (Glaser et al., 2001). Apparently, these dark, nutrient rich soils were created by pre-Columbian people by repeated “slash and burn” process that ultimately incorporated large contents of char in the soil (Steiner et al., 2004). They have been estimated to be aged at least 2000 years before present and have long been continuously beneficial to tropic vegetation despite abandonment by the indigenous population (Lehmann, 2006). Terra Preta soils are rich in charred biomass and possess higher fertility and productivity than their unamended Oxisol surrounding soils which lack the charred material. This suggests that the char might improve plant growth by furnishing the soil with additional organic matter and nutrients.



Figure 3. Soil profile and productivity of Terra Preta soils (*darker soil in the right side*) compared to nearby unamended Oxisols (IBI, 2016).

The “Terra Preta” soils that were regularly amended with biochar and other organic materials (e.g., fish and animal bones, plant tissues, animal feces) have higher pH, are richer in nutrients, and are distinguished by larger microbial populations and more diverse microbial community structure than unamended Oxisols, which are generally acidic and infertile (Liang et al., 2008; Germano et al., 2012; Taketani et al., 2013) as demonstrated in Table 1.

Table 1. Characteristics of Terra Preta soils under various land use types (i.e., secondary forest, grassland and agricultural land), compared to nearby unamended Oxisols (Gul et al., 2015)

Soil chemical characteristics	Terra Preta	Unamended Oxisol
pH	4.1–5.5*	2.6–3.8
Organic C content (g kg ⁻¹)	15.7–31.5*	10.2–21.8
Total nitrogen (mg kg ⁻¹)	10–18	4–16
Total phosphorus (mg kg ⁻¹)	5026–9064*	139–273
Total calcium (mg kg ⁻¹)	40–17545*	50–165
Soil biological characteristics: microbial diversity indices		
Shannon–Weiner	6.08–6.38	5.59–5.66
Simpson	0.004	0.006–0.007
ACE (abundance-based coverage estimators)	1834.0–3523.3	1559.6–1684.5
Sobs	941–1696	820–852
Chao1	1551.1–2736.4	1214.4–1379.9
Singletons	10–17	11–13

Values with an asterisk (*) were significantly different ($P < 0.05$) in Terra Preta soils, compared to unamended soils.

Beneficial properties include higher soil organic matter content, nutrient holding capacity, nutrient content, elevated pH, and water retention (Sombroek 1966; Smith 1980; Glaser et al., 2001). Biochar has also long been used to date archaeological deposits by quantifying its carbon-14 decay (Arnold and Libby, 1951), since biochar and other, more aromatic sorts of black carbon persist in the environment longer than any other form of organic carbon. The persistence and ability to replenish the fertility of highly weathered soils to grow crops in the tropics for thousands of years inspired a vision of a similar, but intentionally designed material to be utilized as a soil conditioner and carbon-storing reservoir.

However, attempts to recreate these soils have largely been unsuccessful (Kookana et al., 2011), and results from field and laboratory studies on the effects of biochars on agricultural productivity are inconsistent and inconclusive, with some studies reporting minimal and even negative effects from biochar addition (Spokas et al., 2012). Variety of agronomic effects of a soil, in presence of biochar, on crop yields have been shown (Glaser et al., 2002; Chan et al., 2007; Steiner et al., 2007; Feng et al., 2014), but the exact mechanism is not fully known. The improvement of crop productivity have been attributed to the increase in soil available nutrients (Asai et al., 2009; Uzoma et al., 2011) and enhanced soil physical properties after the incorporation of biochar (Brockhoff et al., 2010; Akhtar et al., 2014).

3.3. Physical properties of biochar

Biochar is a low-density porous material (Liang et al., 2006) with a very large surface area (Kishimoto and Sugiura, 1985; van Zwieten et al., 2009; Herath et al., 2013). An increase in temperature during pyrolysis has been reported to increase the porosity of biochar (Guo and Lua, 1998) by pushing volatile matter out of the original biomass (Downie et al., 2009). An increase in porosity creates additional capillary soil pores, thus creating additional pathways for water movement and potential water storage while reducing bulk density. A surface area increase is generally attributed to a larger proportion of biochar micropores, which can further promote water adsorption (Vartapetian and Voloshchuk, 1995). Enhanced water adsorption can also be attributed to hydrophilic functional groups on the biochar surface, such as carboxy, hydroxyl, and methoxy groups that form over time, since biochar is typically initially hydrophobic (Cheng et al., 2006; Abel et al., 2013). Increased temperature of biomass pyrolysis thus has the potential to provide water-storing conditions. Moreover, biochar's large surface area attracts small particles and facilitates chemical reactions and its porosity facilitates gaseous exchange.

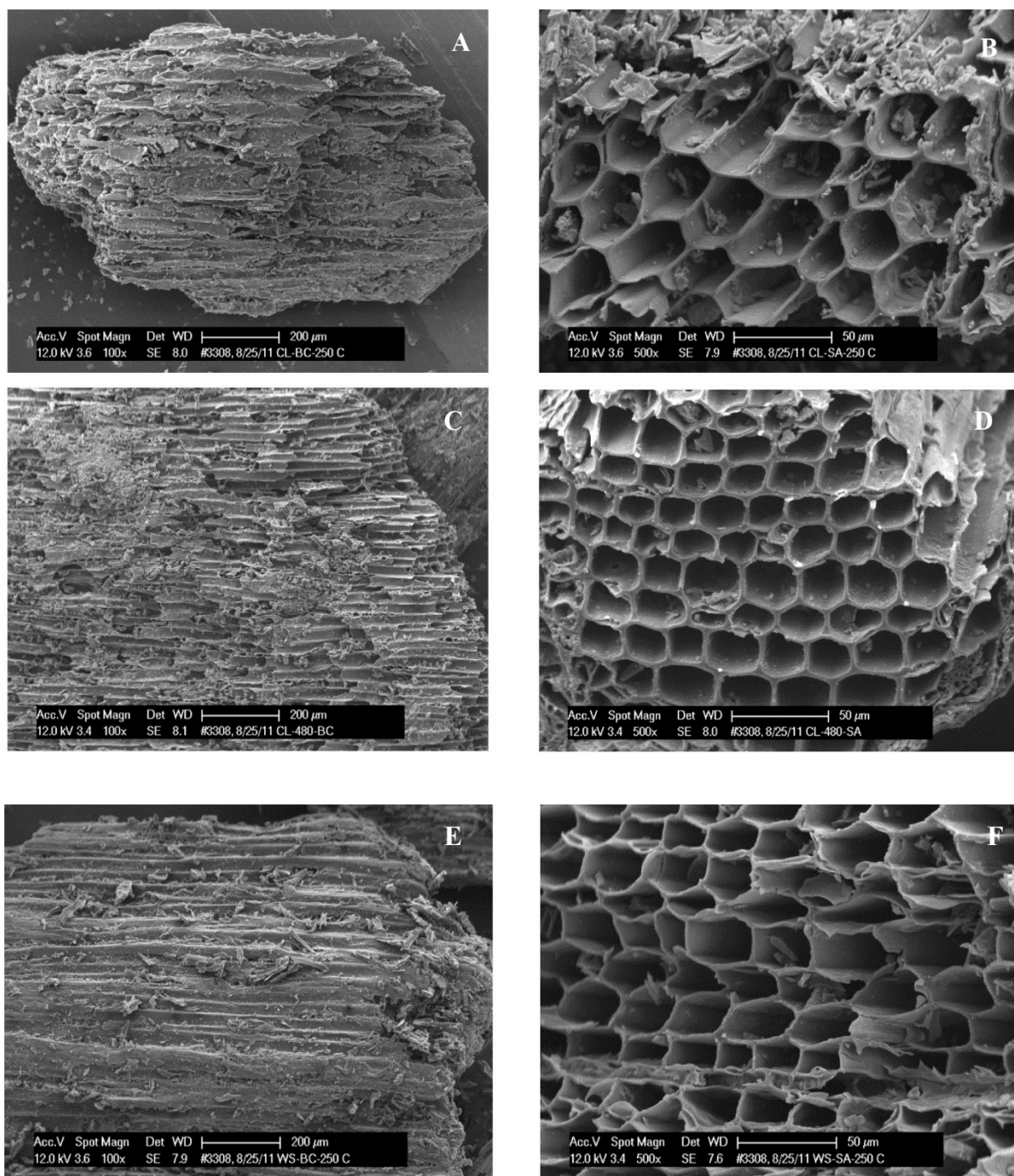


Figure 4. Scanning Electron Micrographs of (A): chicken litter 250 °C biochar; (B): chicken litter 250 °C steam activated biochar; (C): chicken litter 480 °C biochar; (D): chicken litter 480 °C steam activated biochar; (E): wood chip 250 °C biochar; (F): wood chip 250 °C steam activated biochar; (G): wood chip acid activated biochar; (H): wood chip 500 °C biochars; (I): wood chip 500 °C steam activated biochars; and (J): wood chip 500 °C acid activated biochar (Lima et al., 2015).

Little is known about the half-life of biochar due to the recalcitrance of biochar which depends on a multitude of factors, including the type of biomass used for pyrolysis, the production conditions, soil properties, and climate (Lehmann et al., 2006). The pyrolysis conditions and feedstock type both govern the resulting physical and chemical properties of biochar, too (Downie et al., 2009). Fig. 4 shows, as an example, the effect of different pyrolysis temperatures and subsequent activation on the porous structure of biochar.

In addition, pyrolysis temperature controls water repellency. From the viewpoint of improving the available water content in field soil, biochar formed at higher pyrolysis temperatures may be desirable because the biochars formed at lower temperatures are more water-repellent (Kinney et al., 2012).

The matrix of biochar reveals an amorphous structure with crystalline areas (Lehmann and Joseph, 2009) consisting of random polycyclic aromatic (graphene) layers rimmed by functional groups (Zhu et al., 2005) and mineral compounds (Lehmann and Joseph, 2009). The pyrolysis process above 330 °C is associated with the formation of polyaromatic sheets which create turbostratic structures (Keiluweit et al., 2010) and increased porosity. Studies have demonstrated that higher temperatures lead to a decrease in particle size (Downie et al., 2009) and the development of nanoporosity (< 2 nm), which underpins the high surface area of biochar (Downie et al., 2009). In fact, physical properties vary depending upon the biomass feedstock used and the thermochemical conditions of char formation (Fig. 4).

3.4. Effect of biochar on soil physical and hydrophysical properties

Biochar amendment of soil has been proposed for carbon (C) sequestration (Molina et al., 2009; Woolf et al., 2010) and for improving soil productivity (Liu et al., 2013). Additionally, due to its high porosity and larger specific surface area, interest in using biochar to alter the physical and hydraulic properties of the soil is increasing (Downie et al., 2009; Novak et al., 2012; Lei and Zhang 2013; Lu et al., 2014).

The list of physical properties of the soil ranges from the electrostatic forces binding its microscopic particles to the structural cohesion that helps the soil to resist erosion. These properties include bulk density, porosity, aggregate stability, penetrability, tensile strength, and its hydrological characteristics, that is, the way in which it absorbs, retains and releases water. All of these properties control the ability of plant roots to penetrate the soil to obtain water, air and nutrients, and have a direct impact on the chemistry and biology of soils. The factors which control these properties include particle size distribution (texture) and the quantity and quality of soil organic matter.

Studies show that biochar may improve soil's performance by altering soil physical characteristics such as porosity, bulk density, hydraulic conductivity and water holding capacity (Tryon, 1948; Streubel et al., 2011; Githinji, 2013; Herath et al., 2013). This is due to the physical properties of the biochar and the ways in which biochar particles are packed together with the soil particles. Hence, the biochar has the capacity to contribute to the already existing soil texture properties by altering porosity, surface area, and aggregate formation.

The size of biochar particles is also variable and, if undisturbed, typically varies between 0.6-4.75 mm (Downie et al., 2009). Considering the increased porosity and large particle size, biochar can reduce the bulk density of soils, thus improving soil aeration, strength, and water flow processes (Downie et al., 2009; Laird et al., 2010), reduce their tensile strength (Chan et al., 2007) and decrease penetration resistance (Busscher et al., 2010).

Results are mixed, however, and reflect the type of biochar that is used and the type of the soil being treated. Downie et al. (2009) report that biochar has been experimentally linked to improved soil structure or soil aeration in fine-textured soils. Biochar's influences on soil structure and aggregation (Liang et al., 2006) are subtle and are linked to its porosity, granularity and surface charge (Major et al., 2009b). Piccolo et al. (1997) go on to suggest that these effects could increase resistance to erosion. Teixeira and Martins (2003) contrast Amazonian dark earths with similar soil

but lacking biochar additions; as being more granular, workable, porous, structurally resilient and well drained and having lower bulk density, but it is difficult to isolate the effects of biochar from other factors (especially the native soil organic matter) in a historical context and over a large geographical area. More research needs to be done in order to fully understand on how far and well can biochar's influence go.

The presence and stability of aggregates is important for soil's carbon storage ability and structural state. Structurally, aggregates and the spaces between them provide enhanced places for air, water, and microbial movement. The quality of the soil, as a result, increases. The formation of soil aggregates is an important process governed by biological and physico-chemical mechanisms. These processes yield strong micro-aggregates and weaker macro-aggregates ($> 250 \mu\text{m}$), whose strength is dependent on the land management procedures (i.e. tilling, irrigation, etc.) applied. Several studies have showed that aggregate formation has improved when biochar was added unto the soil. However, the mechanism of aggregate formation is still largely unknown (Glaser et al., 2002; Brodowski et al., 2006; Liang et al., 2006; Ibrahim et al., 2013) and not clearly understood. It is suspected that biochar addition provides suitable habitat for biota, stimulating microbial and fungal activity, increasing their exudate production and thus providing greater amounts of binding agents between particles (Six et al., 2002). It is also plausible that aromatic components, which are high in biochar, contribute to stabilization of micro-aggregates (Brodowski et al., 2006). Earthworms have also been observed to mix biochar through soil profiles and promote aggregate stabilization (Topoliantz et al., 2006).

3.4.1. Soil water retention

Plant-available water holding capacity (PAWC) is not equivalent to water holding capacity (WHC). PAWC is the amount of water retained in the soil that can be removed by plants and is estimated by the difference in soil water content between field capacity (FC) and permanent wilting point (PWP) (Radcliffe and Simu, 2010). How much water a soil can hold against gravity is very important for plant growth, but not all of the water held by soil is available for plant growth. WHC is virtually synonymous with water content at field capacity and includes water available to plants

as well as water held below the permanent wilting point, including the water that is sometimes referred to as hygroscopic, being held by surface forces in a layer immediately adjacent to solid particle surfaces (Cassel and Nielsen, 1986). WHC has been shown to change after biochar incorporation (Novak et al., 2009). Biochar was used as a soil amendment to increase WHC of the soil by 11 % (Karhu et al., 2011) while the incorporation of biochar in a sandy loam soil improved WHC by 32 % (Bruun, 2011). There was an increase in WHC but not in PAWC thirty months after field application of acacia green waste biochar (Hardie et al., 2014).

Soil hydraulic functions are important for describing hydrological, ecological and agricultural processes. A commonly reported effect of biochar application to soil is an improvement in soil's capability of water retention (e.g. Sohi et al., 2009; Verheijen et al., 2010; Abel et al., 2013). These results show a huge potential of soils, in presence of biochar, to increase the availability of water to plants. The most widely used method of characterization of hydraulic properties on unsaturated soils is the soil water retention curve (SWRC). Water retention curves are plots of the volumetric water content versus the matric potential (tension) of water contained in the soil. The water retention curves are also related to the unsaturated hydraulic conductivity of the soil. Models of unsaturated flow and transport incorporate soil-water retention curves, which, therefore, may serve as integrated indices of soil quality.

One of the first reports on the effect of biochar on water retention was published by Glaser et al. (2002), who found in his work that Terra preta soils have an increased water retention capacity compared to adjacent soils. Gaskin et al. (2007) confirmed the same result, namely, that biochar can improve soil water retention, reporting a doubling in the mean volumetric water content of a loamy sandy soil at -2 kPa following the addition of peanut hull biochar at a rate of 88 t ha^{-1} . Further research studies, confirmed these effects (in the qualitative sense) for different types of soils (Asai et al., 2009; Sun and Lu, 2014) and for biochars produced from different feedstocks and under different production conditions (e.g., Masulili et al., 2010; Karhu et al., 2011; Basso et al., 2013). However, Hardie et al. (2014) reported no significant effects on soil moisture release characteristics (i.e., the soil water retention curves) or plant-available water contents when a green waste biochar was applied to a clay loam soil.

The large surface area of biochar gives a given soil a water holding capacity (WHC) comparable to clay, while its porosity provides it with the aeration that clay lacks. This means that the effect of biochar on some properties, like infiltration or hydraulic conductivity, varies according to soil texture (Tryon, 1948). As a result, biochar can counteract both the drought prevalence in sandy soils (Uzoma et al., 2011) and the waterlogging prevalence in heavy clay soils (Asai et al., 2009). Glaser et al. (2002) report Amazonian dark earths with field water retention capacity 18 % higher than the surrounding soils without biochar. In various experiments around the world, biochar-amended soils have shown increases in WHC from 11 % to 481 % with the higher values usually occurring on lighter (sandier) soils (Iswaran et al., 1980; Dugan et al., 2010; Karhu et al., 2011; Southavong and Preston, 2011; Uzoma et al., 2011). Kammann et al. (2011) also showed greater water-use efficiency after applying biochar to a sandy soil.

The effectiveness of biochar as a soil amendment in improving plant productivity is determined by the physico-chemical nature of the biochar-soil interaction (Chan et al., 2007; Chintala et al., 2013; 2014). Biochar additions to soils have variously been reported to have neutral, beneficial, and detrimental effects on soil quality (Chan et al., 2009). The reported beneficial effects of biochar include an increase in WHC, improved nutrient retention and availability and reduction in nutrient loss from leaching and runoff events (DeLuca et al., 2009; Major et al., 2009; Karhu et al., 2011). Biochar particle size affects water and nutrient retention potential. Smaller-sized particles have greater surface area, can more easily accommodate within soil matrix pores and thus may more efficiently increase nutrient retention and WHC (Major et al., 2009; Leifeld et al., 2007). Very fine biochar particles are most likely present in biochar materials when small sized feedstock particles have been used (Laird et al., 2010). Biochar is also highly porous and thus its internal pores could add to water storage within soils (Atkinson et al., 2010). Biochar could also affect pore arrangement between particles (Hardie et al., 2014) with corresponding favorable effects on soil water retention.

Another component of the water retention effects of biochar is its influence on gravitational water, that is, on the ability of the soil to drain after overwetting. The expectation is that biochar will reduce drainage in sandy soils, whereas increased drainage will occur in clayey soils (Atkinson et

al. 2010; Major et al. 2010). This effect is not always achieved, because of variable biochar physical properties and rate of application (Barnes et al., 2014).

3.4.2 Hydraulic conductivity

The rate of water movement through soil is important for infiltration, delivery of water to plant roots, and flow of water to streams, groundwater, and oceans (Klute, 1986). The saturated hydraulic conductivity of the soil (K_{sat}) is principally a function of soil's pore size distribution, pore continuity and tortuosity, which all, in turn, depend on soil texture, soil particle packing, clay content, organic matter content, soil aggregation, bioturbation, shrink–swelling, and overall soil structure (Hillel, 1998; Moutier et al., 2000; West et al., 2008). It is also related to fluid properties (e.g., fluid saturation, viscosity, and density) (Freeze and Cherry, 1979). K_{sat} is one of the main physical properties that aids in predicting complex water movement and retention pathways through the soil profile (Keller et al., 2012; Quin et al., 2014), and it is also widely used as a metric of soil physical quality (Reynolds et al., 2000). Sandy soils provide high K_{sat} values, which lead to rapid water infiltration and drainage (Bigelow et al., 2004; Abel et al., 2013). This fast infiltration is advantageous for reducing run-off and rainstorm-event flooding, but it is also an environmental risk, since rapid infiltration rates decrease the time and opportunities for attenuation of concentrations of dissolved nutrients and agrochemicals before reaching groundwater resources (Li et al., 2013).

The impact of biochar on the soil hydraulic conductivity is a result of complex interaction between soil and biochar physical properties. Several studies have reported that the incorporation of biochar to soil increased the saturated hydraulic conductivity (K_{sat}) (Moutier et al., 2000; Oguntunde et al., 2008; Herath et al., 2013), but other studies have observed decreased K_{sat} following biochar additions (Brockhoff et al., 2010; Uzoma et al., 2011; Githinji, 2014). The effects of different feedstock sources, the particle size of the biochar and the rates of its addition have not been exhaustively studied, but it seems evident that the hydraulic impacts are mainly soil-texture dependent (Tryon, 1948). K_{sat} has been observed to increase (Oguntunde et al., 2008; Asai et al. 2009; Herath et al. 2013; Lei and Zhang 2013), decrease (Uzoma et al., 2011; Deveraux et al. 2012;

Barnes et al. 2014), or have no detectable effect (Laird et al., 2010; Hardie et al., 2013). Herath and colleagues (2013) reported increases in the K_{sat} of a corn stover char amended silt loam soil (10-11.3 t/ha), while 20 t/ha black locust char reduced the K_{sat} of a sandy soil in a study by Uzoma et al (2011). Asai et al. (2009) found significant increases in saturated hydraulic conductivity following biochar application to a clay loam soil in an upland rice paddy field in Laos. Hardie et al. (2014) reported a significant increase in the near-saturated hydraulic effects in the soil of an apple orchard following biochar application to sandy loam Planosol (WRB, 2014). The effects of biochars vary with the soil type and feedstock materials as well as the processing conditions of biochar. For example, Laird et al. (2010) did not find significant influence of hardwood biochar on the soil saturated hydraulic conductivity Major et al. (2012) reported no significant effect on either the water holding capacity or the saturated hydraulic conductivity of a clay soil following the addition (20 t ha⁻¹) of a biochar produced from wood. It is important to note that some of the studies which report positive effects have used biochar application rates which are likely to be far higher than what is possible for large scale field applications, such as 195 t ha⁻¹ as reported by Yu et al. (2013).

3.4.3 Water repellency (hydrophobicity)

Soil water repellency (SWR) or hydrophobicity is linked to the presence of non-polar aliphatic and aromatic groups of organic hydrophobic compounds (Ellerbrock et al., 2005). These compounds accumulate in soil due to natural causes such as plant and organic matter decomposition, microbial activity, condensation of organic compounds during vegetation fires or anthropogenic impacts such as oil spills (Roy et al., 2003). The accumulation of these compounds results in coating soil particles, decreases the surface tension and restricts water infiltration at the soil surface (Morley et al., 2005; Koch and Ensikat, 2008).

Several studies in the last two decades reported about the influence of soil water repellency on hydraulic properties (e.g., Bachmann et al., 2013). The soil hydraulic system becomes more complex when biochar is added to soil. Functional surface groups of chars create hydrophobic hot-

spots thereby increasing spatial heterogeneity of the water repellency of the soil (Kinney et al., 2012).

The surfaces of biochar feature water adsorptive, carboxy, hydroxy and methoxy groups, as well as water repellent functional bonds, aliphatic and aromatic nonpolar groups (Chun et al., 2004; Sharma et al., 2004; Baccile et al., 2009). It is reasonable to assume that hydrophobic characteristics of biochars counteract the positive effect of char addition on AWC and hydraulic conductivity. Water repellency and delayed wetting are commonly causing higher fractions of entrapped air and thus decrease the fraction of saturated soil pores, which should reduce both, the AWC and hydraulic conductivity. From the viewpoint of improving the available water content in field soil, biochar formed at higher pyrolysis temperatures may be desirable because the biochars formed at lower temperatures are more water-repellent (Kinney et al., 2012).

4. Materials and Methods

4.1. Location

The experiments were carried out in the laboratory of the Department of Water Resources, Faculty of Agrobiological Sciences, Food and Natural Resources of the Czech University of Life Sciences, Prague.

4.2. Soils

For this research, three soil types were used to investigate the effect of various admixtures of biochar on their physical and hydrophysical properties. The three different soils used were a graded fine silica sand (SA), the Suchdol silty loam Chernozem on loess (CH), topsoil only, and a light Cambisol on paragneiss (CM) from Valečov in the Bohemo-Moravian Highland (topsoil only) (see Table 2).

The biochar used for this laboratory experiment was obtained from Biouhel CZ, s.r.o. It was made from an approximately 1:1 mixture of silage maize rests in a biogas station digestate and wheat straw. The biochar was pyrolyzed at 460 °C for 18 minutes. The fresh biochar had a water content by mass and volume of 0.84 g/g and 0.13 cm³/cm³, respectively. Without any further alteration of the biochar properties, it was stored at room temperature ready for use.

Both Chernozem and Cambisol soils were collected from the 0 to 20 cm depth interval from the experimental field of Czech University of Life Sciences (CULS) in Suchdol, Prague and the experimental field of the Potato Research Institute Havlíčkův Brod, Ltd., research station Valečov, respectively. The Chernozem and Cambisol soils were taken in early spring 2015, when the soil

was broken down into small aggregates due to winter frost, before destruction of this favorable structure by tillage operations and by rains.

The soils were passed through a 5 mm sieve without crushing of the natural aggregates and mildly air-dried and quartered to obtain a number of statistically equivalent samples. The moisture content of the soil samples so obtained was not allowed to dry excessively. The samples were stored in plastic bags in boxes covered against evaporation at room temperature. In this way, the aggregates were supposed to be more stable and not so much prone to slaking, when wetted during the subsequent experiments (see Appendix B and C).

Table 2. Characteristics of the three soils (CH, CM and SA) and the biochar used for this study.

	Chernozem	Cambisol	Silica Sand	Biochar
Soil type (WRB 2014)	Haplic Chernozem*	Dystric Cambisol	Artificial	Artificial
Soil substrate or raw material	Loess*	Paragneiss	Sandstone	Maize biogas digestate and wheat straw
Textural class (NRCS USDA)	Silty loam*	Sandy loam***	Fine sand	
Altitude (m)	281	445		
Longitude	14°22'25"E	15°29'30"E	15°15'11"E	
Latitude	50°07'40"N	49°39'30"N	50°29'50"N	
Average annual precipitation (mm)	431**	660***		
Mean annual temperature (°C)	9.3**	7.2***		
Bulk density (g/cm ³)****	1.08	1.28	1.50	0.15
Particle density (g/cm ³)*****	2.797	2.854	2.650	1.097
Initial water content by mass (%)	5.960	1.243	0.058	84.010

* *Kodesova, 2011*

** *Meteorological Station of CULS, measurements of 2004–2016 (Meteostation CULS, 2016).*

*** *F. Doležal, 2016, personal communication*

****The bulk density of the soils and the biochar were measured by filling the 250 cm³ rings without compaction till the edge of and putting them in oven for 24 hours at 105 °C. The weight of the soils before and after oven drying were measured.

***** The procedure for the particle density measurement of the soils and biochar is described in detail in section 4.4.4.

The silica sand soil used for this study was bought from the company Sklopísek Střeleč, a.s., Czech Republic, under commercial name ST 56. It was obtained by grinding and subsequent sieving of silicic sandstone. Around 99.0 % of its mass consists of silica (silicon dioxide). The detailed characteristics of this soil, can be seen in table 2 & 3 and Appendix A.

For all three soils and biochar, homogenization for uniformity was separately done by coning and quartering, so when subsamples were taken from the large samples for a particular analysis (see Appendix B). It is a method used by analytical chemists to reduce the sample size of a powder without creating a systematic bias. The technique involves pouring the sample so that it takes on a conical shape, and then flattening it out into a cake. The cake was then divided into quarters; two quarters which sit diagonally opposite one another were combined and stored separately from the other two which were also combined. The same process was continued until samples of an appropriate sample size remain. Large pieces of paper were needed for this purpose (to be put on the floor). Once quartered, the particular subsamples were stored in plastic bags for future use.

Table 3. Chemical analysis of the fine silica sand, ST 56, with Roentgen - fluorescent analysis (RFA) (Sklopísek Střeleč, a.s., 2015)

No	Chemical Compound	% *
1	SiO ₂	99.0
2	Fe ₂ O ₃	0.09
3	K ₂ O + Na ₂ O	0.2
4	CaO + MgO	0.2

* The above-mentioned information is based on average values.

The basic approach was to mimic approximately the situation in the field immediately after cultivation, when the soil is loose, after first few rains. Therefore, the soil samples were not compacted or only very lightly compacted before all sorts of hydraulic testing, except that spontaneous collapse of the powdery soil occurred during the initial capillary wetting of the sample.

4.3. Treatments

The experiments include the three soils types mixed with the biochar. The biochar concentration variants used in this study were (mass of air-dry biochar / mass of air-dry soil): control treatment (soil only, no admixture of biochar); treatment with addition of 0.001 g/g and treatment with addition of 0.01 g/g. Each treatment was carried out in triplication. Only biochar without soil was used in order to determine the dry bulk density and the particle density of the biochar.

For all of the experiments, the appropriate method for preparing the soil-biochar mixtures were tested for the three soils. This was with “blind” samples, the concentration of biochar is zero. After all physical analyses, the remaining soil samples were let to dry and then stored in a plastic or paper bag on which the type and the serial number of the analysis were written, for any later inspection and/or re-analysis.

4.4. Sample preparation

4.4.1. Soil sorptivity determination

Mini Disk Infiltrometer (Decagon Devices, Inc.) was used for measuring sorptivity of the soils and their mixtures with biochar. The Mini Disk Infiltrometer infiltrates water at a suction range of -0.5 to -6 cm through a sintered stainless steel disc having 2.25 cm radius and 3mm thickness. The infiltrometer has small dimensions, having 32.7 cm total length, 3.1 cm diameter of tube, 21.2 cm

water reservoir length and 28 cm the Mariotte tube length. The setting up of the Mini Disk Infiltrometer was made according to the instructions in the manual (Decagon Devices, Inc., 2016). The determination of soil sorptivity was carried out according to the methodology of Zhang (1997). Infiltration was done either by water and ethanol. The suction control tube was set to -5 cm and kept the same for all infiltration experiments with water. However, the tension applied during measurements of infiltration rates with ethanol was 2.5 times lower, i.e. -2 cm, as theoretically substantiated and used by Lamparter et al. (2010). The ethanol (96.6 %) was used to measure the intrinsic hydraulic properties of the soil without the influence of water repellency since almost all soils shows water repellency to some degree (Doerr et al., 2006) and there is an initial hydrophobicity of biochars (Cheng et al., 2006; Baccile et al., 2009; Abel et al., 2013), especially those produced through slow pyrolysis (Kinney et al., 2012; Gray et al., 2014).

For the experiments, three flat ceramic dishes with a diameter about 23 cm were used. All dishes with the soil samples were marked separately with a number and their tare masses were obtained by weighing. Dry soil samples were poured into each dish without any compaction. A filter paper was put on the bottom under the soil. The soil surface was approximately horizontal and smoothed slowly/gently forming a soil layer about 3 cm high, again without any compaction. Detailed experimental setup is shown in Appendix D.

Capillary rise was used to moisten the soil in the dish from the bottom prior to the Mini Disk infiltration experiments. A thin layer of tap water, about 2 mm thick, was created at the bottom of the dish using an access metallic cylinder (a soil core sampler). The water layer spread all over the dish bottom in the basal filter paper and in the bottom about 1 mm of the soil to enable the capillary rise of water into the entire thickness of the soil in the dish. It took a different duration of times before the soil got wet enough and did not take in water anymore (see Appendix E, F and G). Then the dishes with the wet soil were weighed again to determine the amount of water added in order to determine the initial soil water content. Nothing was added and cut from the dishes after the saturation of the soils in the dishes through capillary rise. The the dish was left standing on the laboratory desk for about a week to reassume approximately its pre-wetting water content. Three

parallel dishes with different soil types and treatments for the mini disk infiltration measurement were used. In each dish, two short-lasting water infiltration experiments were done and two other with ethanol, one experiment after another, using a single Minidisk, at four different spots distributed homogeneously around the circumference of the dish. It was assumed that mutual interference of neighbouring infiltration experiments in the same dish and also the effect of divergence of flow in the soil near the bottom of the dish can be minimised and neglected, if the duration of each experiment is kept short enough and the amount of water infiltrated is small enough. This procedure was chosen in order to minimise the amount of the soil needed for the experiments. The duration of individual experiments varied according to the infiltration capacity of the soil between about 15 seconds (for silica sand) and about 5 minutes (for Cambisol). The optimum length of the infiltration experiment was determined after some experience. The ethanol used was bio-ethanol 96.6 %, denaturated by 1 % of 2-butanone (methyl ethyl ketone). It was recommended for use in soil physics by Lamparter et al. (2010).

At the end of each measurement, soil samples were taken into aluminium soil moisture samplers from the wetted zone beneath the disk of the infiltrometer for the purpose of estimation of the final soil water content.

The tension applied during the measurements was 5 cm and 2 cm for water and ethanol respectively. Cumulative infiltration and time measurements were registered in the data record form for the mini disk infiltrometer suggested by Bátorová et al. (2013). As the process was very quick, it was necessary to record the process photographically, using a digital video camera, and only then to transfer the records onto paper by inspecting the video.

To determine the sorptivity of the dry soils, the simple method proposed by Zhang (1997) was used. The method requires fitting of the results to the equation (1), formally resembling the Philip (1957) equation for one-dimensional infiltration:

$$I = C_1 t + C_2 \sqrt{t} \quad \text{-----} \quad (1)$$

where C_1 ($L T^{-1}$) and C_2 ($L T^{-1/2}$) are parameters, . C_1 being related to the soil hydraulic conductivity, and C_2 to the soil sorptivity, I (L) is the cumulative infiltration, and t (T) the time.

If the infiltrometer is placed on the surface of a relatively deep and homogeneous soil and the infiltration lasts long enough (which was not our case), the hydraulic conductivity of the soil, K , at the particular applied tension h can be computed from equation (2).

$$K(h) = \frac{C_1}{A} \quad \text{-----} \quad (2)$$

where C_1 is the slope of the curve of the cumulative infiltration versus the square root of time, and A is a value depending on the van Genuchten parameters of the soil water retention curve (van Genuchten, 1980), the applied suction and the radius of the infiltrometer disk. The values of A can be obtained from table 4 or can be computed from equations (3) and (4) using the van Genuchten parameters n (-) and α (L^{-1}), listed in table 4:

$$A = \frac{11.65(n^{0.1}-1)\exp[2.92(n-1.9)\alpha h]}{(\alpha r_d)^{0.91}} \quad \text{for } n \geq 1.9 \quad \text{----} \quad (3)$$

$$A = \frac{11.65(n^{0.1}-1)\exp[7.5(n-1.9)\alpha h]}{(\alpha r_d)^{0.91}} \quad \text{for } n < 1.9 \quad \text{----} \quad (4)$$

where r_d (L) is the disk radius and h (L) is the applied suction at the disk surface.

Table 4. Van Genuchten parameters for 12 soil texture classes and values of A for the Minidisk Infiltrometer with suction values from 0.5 to 7 cm (Decagon Devices, Inc., 2016).

	radius	2.25	A							
	alpha	n /ho	-0.5	-1	-2	-3	-4	-5	-6	-7
sand	0.145	2.68	2.84	2.40	1.73	1.24	0.89	0.64	0.46	0.33
loamy sand	0.124	2.28	2.99	2.79	2.43	2.12	1.84	1.61	1.40	1.22
sandy loam	0.075	1.89	3.88	3.89	3.91	3.93	3.95	3.98	4.00	4.02
loam	0.036	1.56	5.46	5.72	6.27	6.87	7.53	8.25	9.05	9.92
silt	0.016	1.37	7.92	8.18	8.71	9.29	9.90	10.55	11.24	11.98
silt loam	0.02	1.41	7.10	7.37	7.93	8.53	9.19	9.89	10.64	11.45
sandy clay loam	0.059	1.48	3.21	3.52	4.24	5.11	6.15	7.41	8.92	10.75
clay loam	0.019	1.31	5.86	6.11	6.64	7.23	7.86	8.55	9.30	10.12
silty clay loam	0.01	1.23	7.89	8.09	8.51	8.95	9.41	9.90	10.41	10.94
sandy clay	0.027	1.23	3.34	3.57	4.09	4.68	5.36	6.14	7.04	8.06
silty clay	0.005	1.09	6.08	6.17	6.36	6.56	6.76	6.97	7.18	7.40
clay	0.008	1.09	4.00	4.10	4.30	4.51	4.74	4.98	5.22	5.48

In our case, however, we focused on the infiltration parameter C_2 ($L s^{-1/2}$) in order to estimate the sorptivity of the soil or its mixture with biochar. The sorptivity S ($L s^{-1/2}$), which is the ability of the soil to absorb water without the influence of gravity, can be obtained according to Zhang (1997) from the parameter C_2 in a similar way as the hydraulic conductivity from the parameter C_1 (see equations (2) to (4) above):

$$S = \frac{C_2}{A_2} \text{-----} \quad (5)$$

where

$$A_2 = \frac{1.4b^{0.5}(\theta_o - \theta_i)^{0.25} \exp[3(n-1.9)\alpha h]}{(\alpha r_d)^{0.15}} \quad \text{---- (6)}$$

The parameter b can be taken as 0.55, θ_o is the soil water content at the suction h , θ_i is the initial soil water content and the other symbols have the same meaning as above. In our case, we assume that A_2 is approximately constant, so that we can compare directly C_2 instead of the sorptivity S .

The estimation of C_2 from the equation (1) is more difficult than the estimation of C_1 . There are several irregularities and sources of error encountered during the measurement, such as non-negligible time of travel of air bubbles from the bottom of the infiltrometer to its top, an imperfect and variable contact between the soil and the porous plate of the infiltrometer, water repellency of the soil (causing that it takes some time before water gets “courage” to enter the soil), too shallow a layer of the soil in the dish, the soil already partly wetted by previous infiltration run in the same dish, etc. Two special provisions therefore had to be taken:

- a) We selected only some suitable points and not the whole curve for the fitting.
- b) We added a third parameter to fit, namely, the time offset t_0 .

The purpose of the fitting is to let the fitting curve (1), in which $(t - t_0)$ is placed instead of t alone, approximate as tightly as possible the selected points. This is done by the method of least squares, but visual inspection is necessary to confirm that the fitting is good enough. During the fitting procedure, we inspect two graphs at the same time, namely, the graph $I(t)$ and the graph $I(\sqrt{t})$. It is required that:

- a) the fitting curve passes through the selected points or near to them,
- b) all three parameters (t_0 , C_1 and C_2) are positive and the values of the parameter C_2 for two parallel runs (the same soil, liquid, biochar admixture) are not much different,
- c) the curve $I(t)$ is concave (convex downwards), at least in the region of selected points, and its curvature is largest on the left side of the graph (near the start of the infiltration run),

- d) the curve $I(\sqrt{t})$ is more or less a straight line in the region of the selected points,
- e) the selected points are chosen mainly in the left part of the graph (near the beginning),
- f) the fitting curve runs mostly above the measured points in the region of larger times.

Often, not all of these requirements can be fulfilled.

The critical phase of the process is the selection of points to fit. This has to be usually done several times, unless the fitting gives a satisfactory result. The technique used was the non-linear optimisation by minimising the sum of squared differences between the measured cumulative infiltration I and the cumulative infiltration calculated according to the equation (1) with $(t - t_0)$ instead of t , for the same time t . The optimisation is done in MS Excel using the Solver routine.

4.4.2. Saturated hydraulic conductivity determination

UMS KSAT device (UMS GmbH.), see Fig. 5, was used to measure the soil saturated hydraulic conductivity on artificially prepared soil samples. The KSAT device enables very precise measurements of saturated hydraulic conductivity of soils either by constant head or falling head method based on Darcy's law. Registration and evaluation of the measurements is done automatically by the software KSAT View (UMS GmbH., 2013).

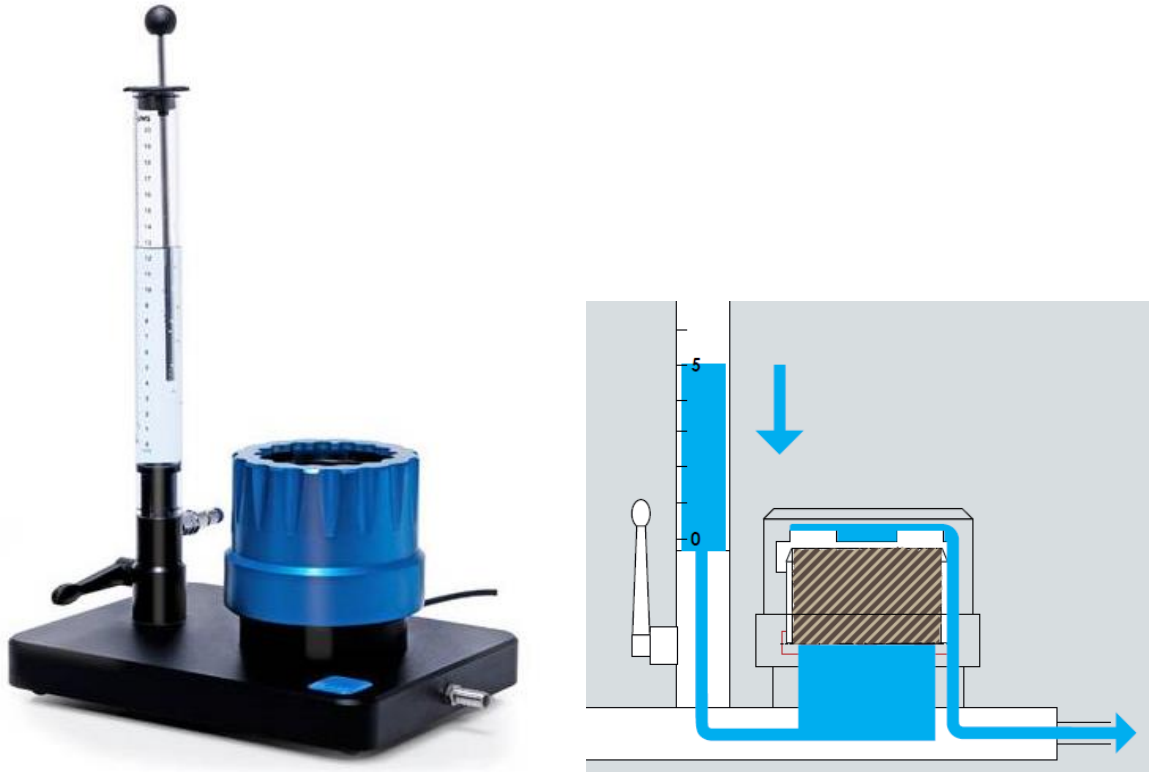


Figure 5. KSAT device (KSAT operation manual; UMS GmbH., 2013).

The soil sampling rings with a volume of 250 cm^3 (50 mm in height and 39.89 mm in radius) were used for the measurements. The air dry soil was poured into each ring without any compaction (only the silica sand had to be slightly compacted). The lower opening of the ring was covered with geotextile and tied to the ring by a rubber band to prevent the loss of the soil through the sampler bottom.

Saturation of the soil samples was carried out by placing the rings on a wet porous plate with a filter paper on it and let the tap water rise by capillary forces into the entire thickness of the soils. The samples were kept on the saturation mat for about 24 hours to ensure maximum saturation. After the saturation, some soils collapsed a little bit, so the surface of the soil in the rings sank below the upper edge of the rings (as already mentioned, the only compaction envisaged was the one due to wetting and spontaneous collapse). If this happened, additional dry soil was poured into the rings (without compaction) on the top of the existing wet soil and let to soak by capillarity. This procedure was repeated until there was enough soil in the rings. After saturation, the surplus of the

soil was carefully removed by a sharp knife, which made the volume of the soil in the rings exactly the same as the internal volume of the rings. No soil was allowed to protrude out through the lower side of the rings, either. In order to achieve this, the rings were put on a glass plate during the cutting off the surplus soil from their top.

The silica sand core samples had to be compacted because the sand is structureless. Hence, 370 g of dry soil was packed into the volume of 250 cm³ ring to reach the dry bulk density 1.48 g/cm³. As the dry sandy soil was very difficult to pack, 10% by mass of water was added to the sample. The soil sample and water were uniformly mixed in a ceramic dish. The appropriate mass of moist sand (370 g + 0.1*370 g = 407 g) was then packed into each of the rings. To ensure both uniformity and the intended density of the soil in each ring, the required amount of soil was compacted gently, starting from the bottom layer, simultaneously for all parallel samples in a particular experiment.

After the capillary saturation, the samples were additionally saturated by immersion in water as required by the KSAT operation manual (UMS GmbH., 2013), see Fig. 6.

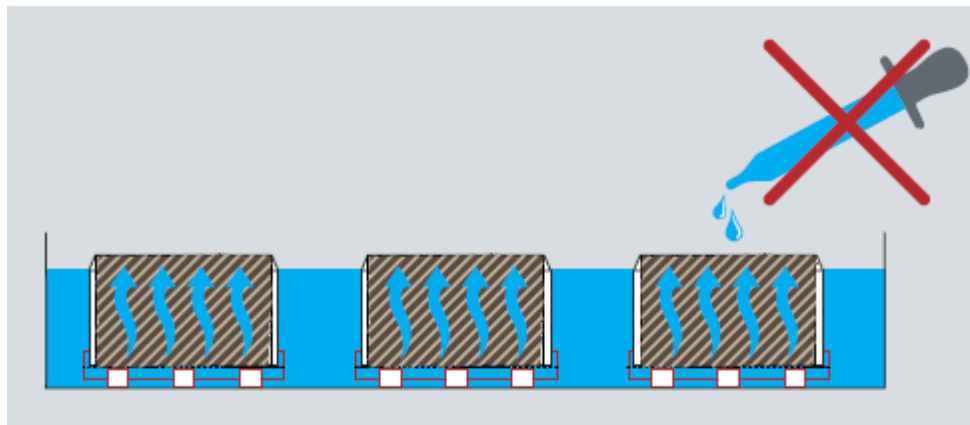


Figure 6. Immersion method of saturating the soil core samples (KSAT operation manual; UMS GmbH., 2013).

The measurements were carried out by employing the falling head method. Three replicates were carried out for each soil type and each biochar concentration, 27 samples in total. Each sample was measured several times in the device to ensure complete saturation.

At the end of the measurement, the samples without the rubber bands were put in the oven and on watch glasses (the mass of each watch glass was ascertained beforehand) and dried at 105 °C. Then they were let to cool down and weighed again to obtain the actual dry bulk density of the wet soil.

4.4.3. Soil water retention curve measurement

The evaporation method according to Schindler and Müller (2006) was used for soil water retention evaluation. The device HYPROP (UMS GmbH) was used to determine the soil water retention curve in the moist range of the curve (between 0 and approx. pF 3, while the soil water matric potential sensors MPS-2 (Decagon Devices Inc.) were used to determine the dry range of the curve (approx. between pF 2.5 and 4.5). In both cases, the method consists of parallel measurement of the soil water matric potential (by microtensiometers in the HYPROP device and the MPS-2 sensor in a container with the soil) and the soil water content by gravimetric method (by weighing the whole sample).

The soil water retention curve was determined only for the silica sand and its mixtures with biochar (0.0, 0.001 and 0.01 g/g). The retention curves of the other soils could not be measured, because the devices were occupied by measurements for other purposes.

Description of the soil water retention curve measurement using HYPROP

Two replicates of each biochar concentration level were prepared, six samples in total. The core samples of 250 cm³ were used. The samples underwent the saturated hydraulic conductivity measurement on the KSAT device (as described above) prior to their processing on the HYPROP device. This procedure follows the recommendation of the manufacturer.

The preparation of the HYPROP device for the measurement is described in details in the HYPROP operation manual (UMS GmbH., 2010). The most important is good degassing of the HYPROP unit and of the microtensiometers. It was done by combining a vacuum pump with manual degassing by syringes.

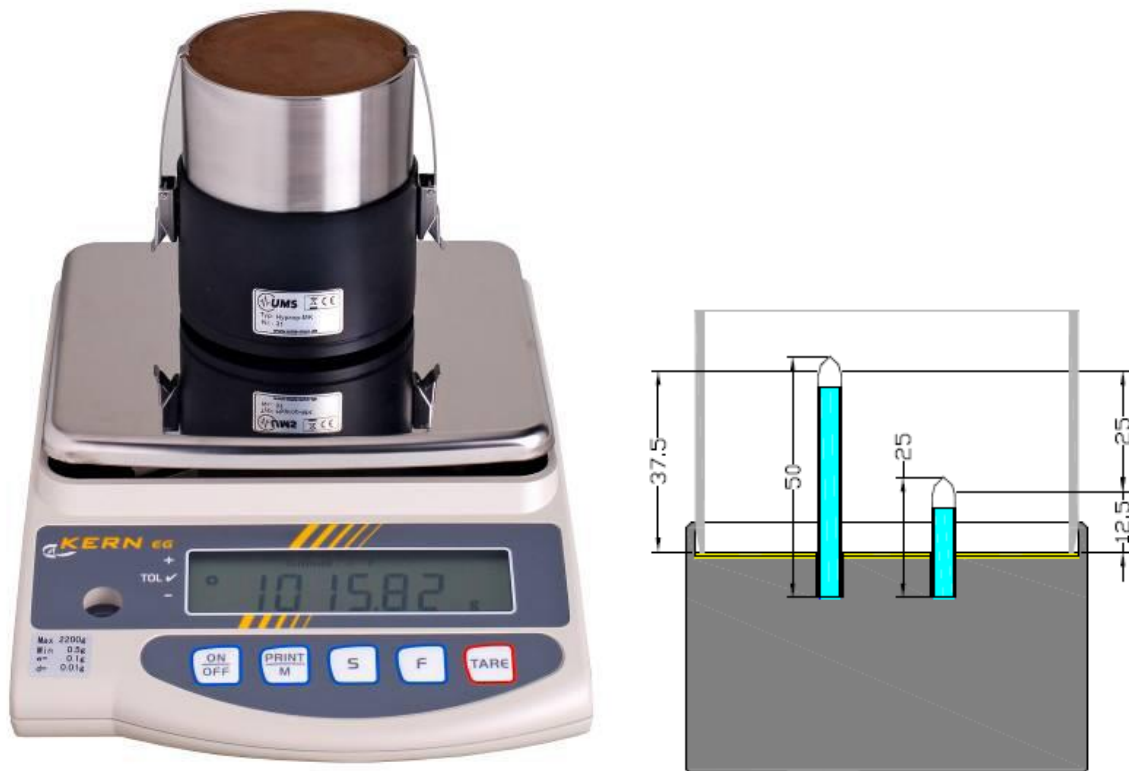


Figure 7. HYPROP device. The position of the microtensiometers at the HYPROP unit (HYPROP operation manual; UMS GmbH., 2010).

Data processing

The raw data were taken from the software tensioVIEW v. 01/2010 (UMS GmbH., 2010) and further processed in MS Excel. The data of the soil matric potential in hPa were converted into the pressure head h (cm) data, using the following equation (7). The data on the mass of the soil were converted into the soil water content. The soil water retention curves (or pF curves) were plotted and evaluated.

$$h = \frac{p}{\rho g} \text{-----} \quad (7)$$

where p is the pressure (Pa), ρ is the density of water (1 g/cm³ at 20 °C) and g is the acceleration due to gravity (9.81 g/cm²).

Description of the soil water retention curve measurement using MPS-2 soil water potential sensors

The MPS-2 soil water potential sensor is primarily designed to take data in the field. The sensors used in this thesis were not individually calibrated. I relied on the information of the manufacturer about their reliability and universal use. In this case, too, the evaporation method was applied. Three sensors were placed into a dish with a homogeneously moistened soil. The dish was permanently placed on the scale. The position of the cables of the sensors was fixed and the water was let to evaporate freely into the laboratory atmosphere. The sensors were saturated prior to the measurement. Basic information about the experimental setup is given in Table 5. The matric potential (and the temperature, in addition) were registered using the EM50 Datalogger (Decagon Devices Inc.) and downloaded by the software ECH2O Utility. The mass of the soil was registered using the scales Kern (max. 810 g) connected to a computer and operated by the software DasyLab, version 9.0. Both measurements were taken simultaneously every 30 minutes. At the end of the

measurement, all soil was quantitatively replaced to a porcelain bowl and dried in the oven at 105°C to a constant mass.

Table 5. Experimental setup for MPS-2 sensors soil water retention measurement.

Concentration of biochar (g/g)	0.0	0.001	0.01
Initial soil water content (cm ³ /cm ³)	0.198	0.205	0.314
Mass of dry sand (g)	512.45	501.06	531.96
Estimation of dry bulk density of the sand (g/cm ³)	1.30	1.27	1.30

Data processing

The data of the soil matric potential in kPa were converted to pressure heads h (cm) using the equation (5). The mass of the soil was converted to the soil water content by volume. The soil water retention curves (or pF curves) were plotted and evaluated.

4.4.4. Particle density determination

The particle density of the soils was measured by the water pycnometer method according to a standard procedure. The particle density of biochar was determined by the water pycnometer method as well, because no other equipment was available. However, some changes in the procedure were made, as demanded by the hydrophobic characteristic of the biochar. Ethanol was used instead of water. First, the density of the ethanol was determined using the same pycnometer, and the density thus obtained was further used in the adjusted formula equation (8). About 3 g of

the biochar was used for the 100 ml pycnometer. Dry matter of the biochar was obtained by drying the air dry biochar at 60 °C in the oven. The biochar samples were saturated for 30 min in ethanol without heating or other treatments, being only mixed with a glass rod. The pycnometers were further tempered to 20 °C and weighed.

$$\rho_z = \frac{m_s}{(m_1 + m_s) - m_2} * \rho_e \text{ ----- (8)}$$

where: ρ_z is the soil particle density (g/cm³),

m_1 is the mass of the pycnometer filled with water (g),

m_2 is the mass of the pycnometer filled with soil sample and water (g),

m_s is the mass of the dry soil sample (g), and

ρ_e is the density of the ethanol (determined for this study as 0.7876 g/cm³)

5. Results

5.1. Sorptivity

The coefficient C_2 in the equation

$$I = C_1 (t - t_0) + C_2 \sqrt{(t - t_0)} \quad \text{-----} \quad (9)$$

was obtained from the Minidisk infiltration measurements as described above. The basic results are presented in Table 6 below and in Figs. 8 to 13.

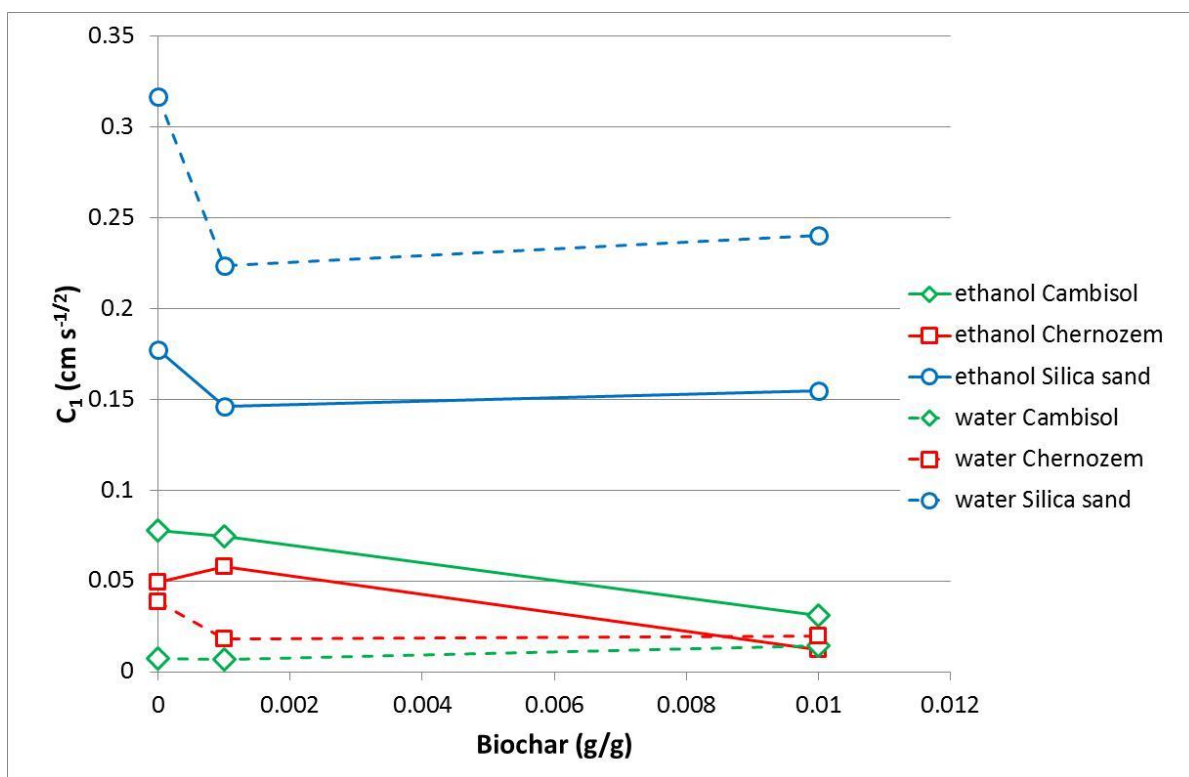


Figure 8. Average values of the coefficient C_2 (a proxy to sorptivity) – all data

Table 6. Basic results of the Minidisk infiltration measurements

Soil	Biochar concentration (g/g)	Liquid	C_2 (cm s ^{-1/2})
Cambisol	0	ethanol	0.06304318
Cambisol	0	ethanol	0.092075379
Cambisol	0.001	ethanol	0.097272707
Cambisol	0.001	ethanol	0.051523717
Cambisol	0.01	ethanol	0.029288536
Cambisol	0.01	ethanol	0.0324747
Chernozem	0	ethanol	0.029106152
Chernozem	0	ethanol	0.069593288
Chernozem	0.001	ethanol	0.053035645
Chernozem	0.001	ethanol	0.063031342
Chernozem	0.01	ethanol	0.023791755
Chernozem	0.01	ethanol	4.32485E-05
Silica sand	0	ethanol	0.255001238
Silica sand	0	ethanol	0.0994487
Silica sand	0.001	ethanol	0.193765497
Silica sand	0.001	ethanol	0.098439479
Silica sand	0.01	ethanol	0.154573771
Silica sand	0.01	ethanol	Not done
Cambisol	0	water	0.010505653
Cambisol	0	water	0.0042077
Cambisol	0.001	water	0.008390368
Cambisol	0.001	water	0.005011512
Cambisol	0.01	water	0.017640776
Cambisol	0.01	water	0.011071582
Chernozem	0	water	0.028608508
Chernozem	0	water	0.048545147
Chernozem	0.001	water	0.01123642
Chernozem	0.001	water	0.024980344
Chernozem	0.01	water	0.023373629
Chernozem	0.01	water	0.016431262
Silica sand	0	water	0.200260038
Silica sand	0	water	0.433407235
Silica sand	0.001	water	0.173731078
Silica sand	0.001	water	0.273854783
Silica sand	0.01	water	0.225649981
Silica sand	0.01	water	0.255001583

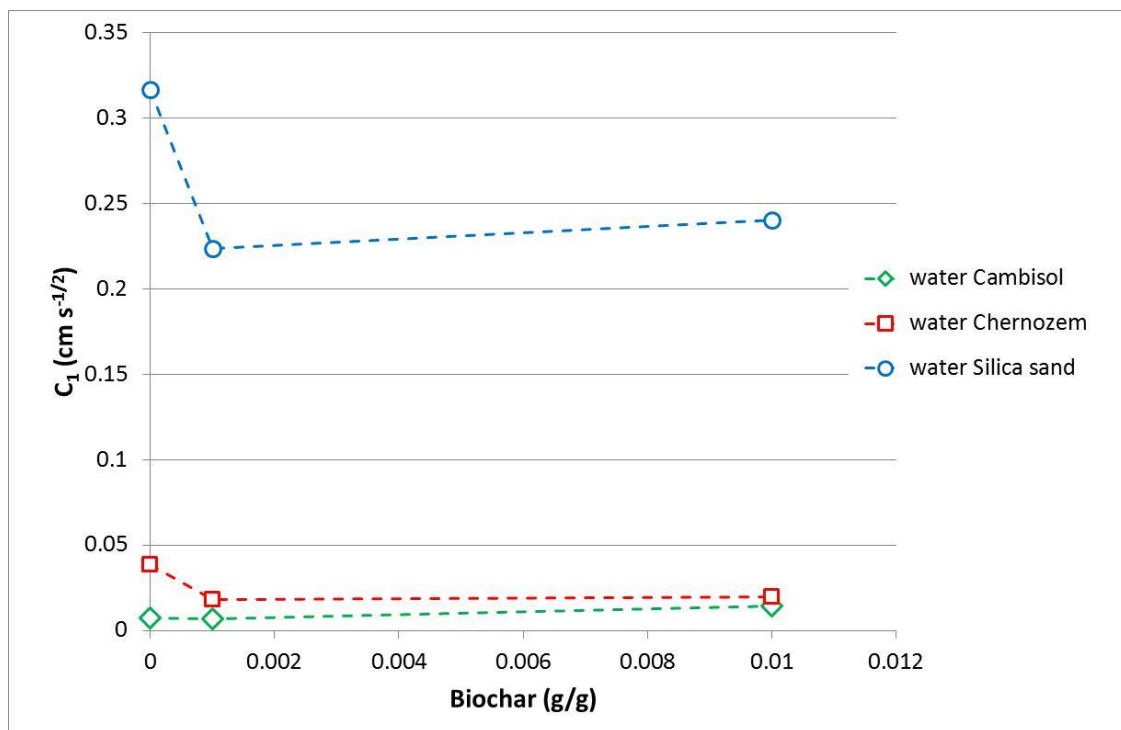


Figure 9. Average values of the coefficient C_2 (a proxy to sorptivity) – water infiltration

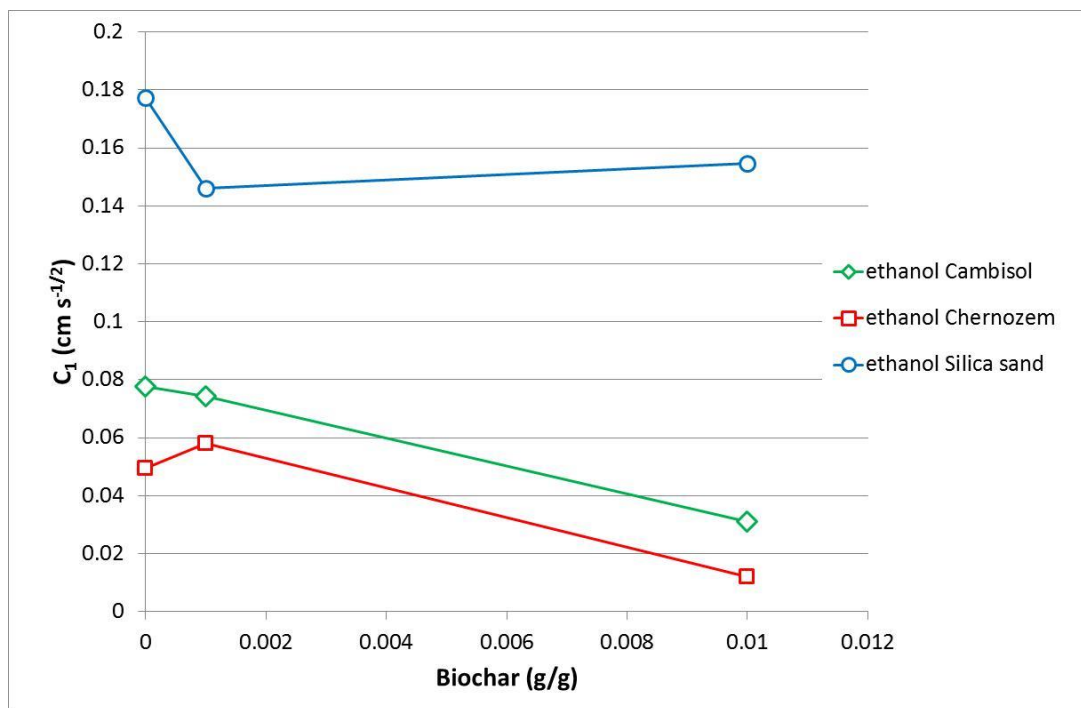


Figure 10. Average values of the coefficient C_2 (a proxy to sorptivity) – ethanol infiltration

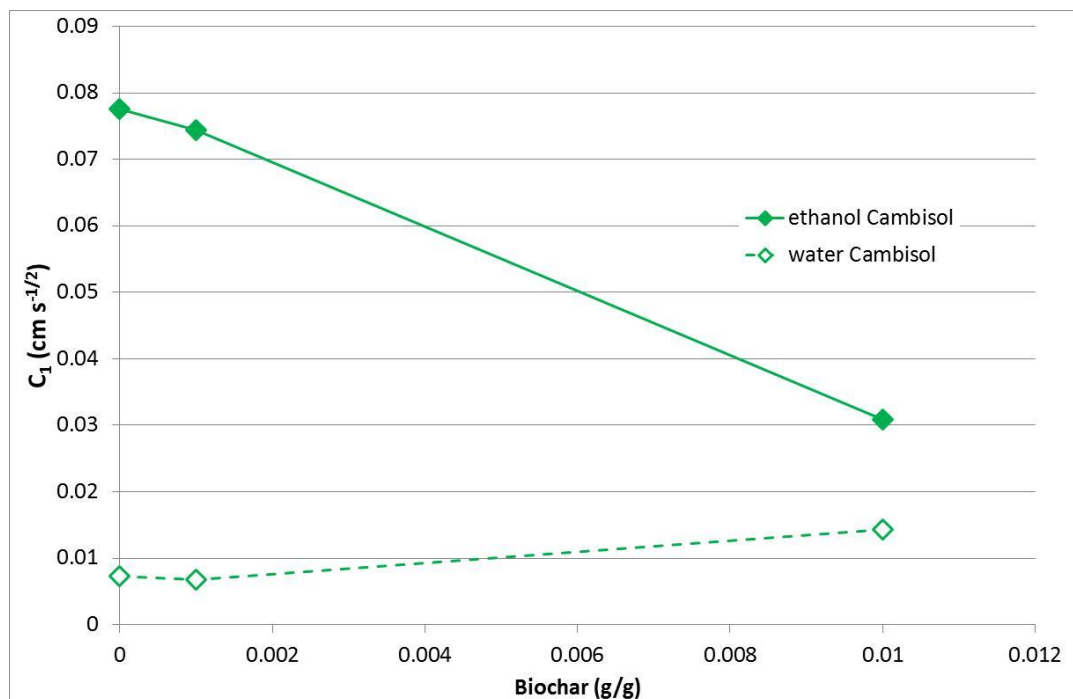


Figure 11. Average values of the coefficient C_2 (a proxy to sorptivity) – Cambisol

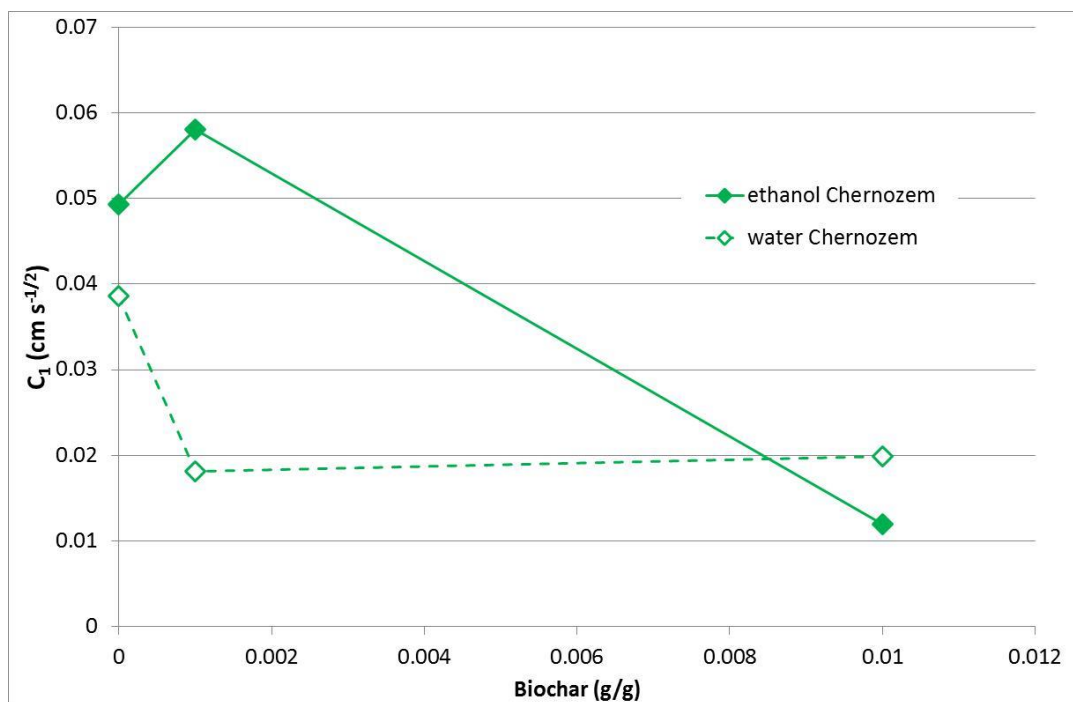


Figure 12. Average values of the coefficient C_2 (a proxy to sorptivity) – Chernozem

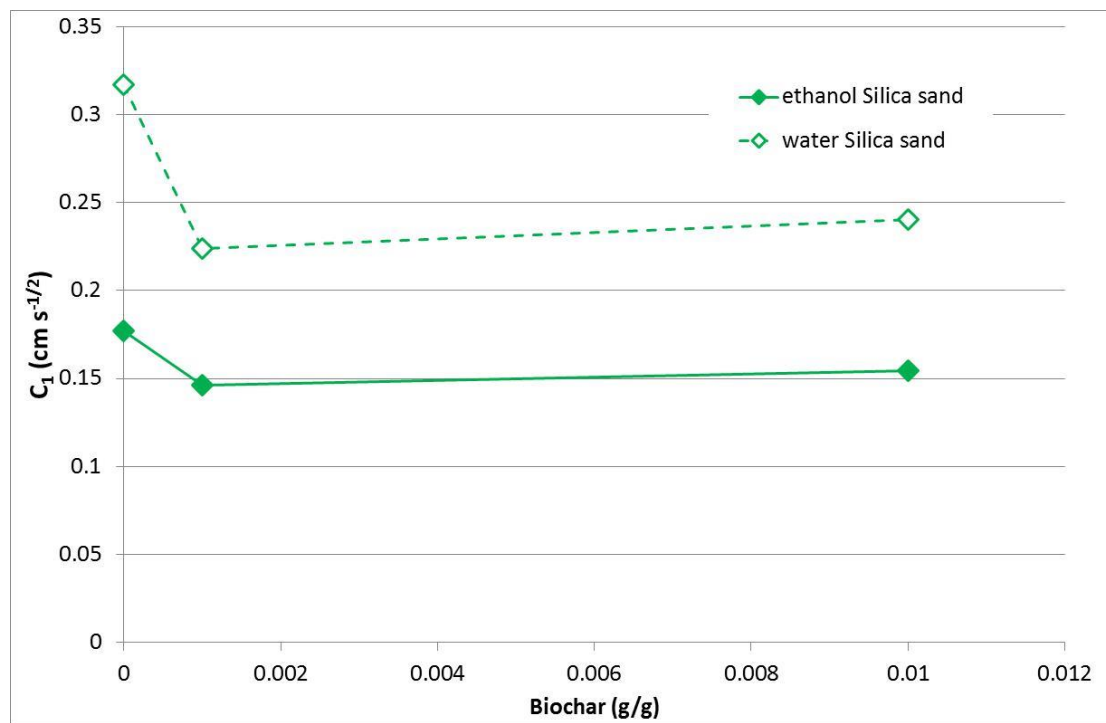


Figure 13. Average values of the coefficient C_2 (a proxy to sorptivity) – Silica sand

5.2. Saturated hydraulic conductivity

Several repeated measurement were done on each sample (= replication). The following Table 7 shows the averages over all measurements made with particular samples, and their standard deviations.

Table 7. Average saturated hydraulic conductivity of the overall measurements

Biochar	Repli- cation	Cambisol		Chernozem		Silica sand	
		Average	St.dev.	Average	St.dev.	Average	St.dev.
Control - no admixture (B0)	1	6.7E-06	7.42E-07	0.000148	2.36E-06	7.41E-05	4.74E-06
	2	1.01E-05	1.36E-06	0.000202	7.03E-06	3.75E-05	1.84E-06
	3	Not done	Not done	0.000235	1.77E-05	4.64E-05	1.11E-06
Biochar 0.0001 g/g (B1)	1	9.78E-06	1.64E-06	0.000241	1.99E-05	0.000126	1.29E-05
	2	1.18E-05	4.3E-06	0.000319	1.74E-05	0.000102	4.02E-06
	3	1.16E-05	9.48E-07	0.000203	6.36E-06	Not done	Not done
Biochar 0.001 g/g (B2)	1	6.69E-06	1.62E-06	0.00017	1.07E-05	2.63E-05	1.48E-06
	2	5.08E-06	4.27E-07	0.000334	1.95E-05	4.32E-05	1.91E-06
	3	9.07E-06	2E-06	0.000254	2.21E-05	6.15E-05	8.88E-07

The replication averages are also plotted in Fig. 14, while the averages over replications can be seen in Fig. 15.

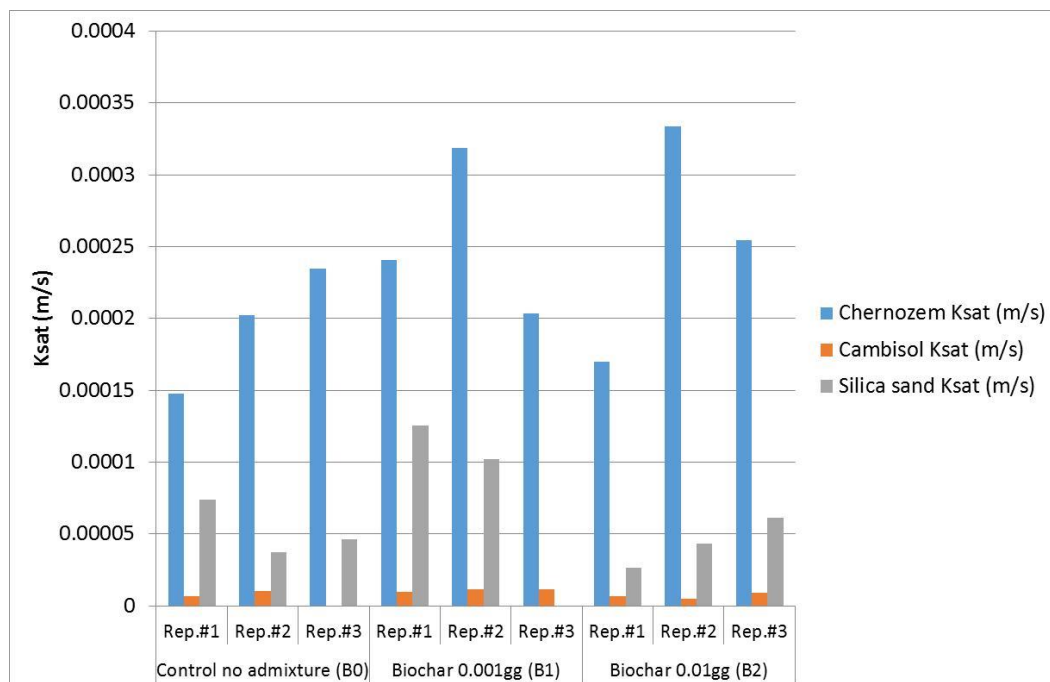


Figure 14. Averages of repeated hydraulic conductivity measurements of individual samples (replications)

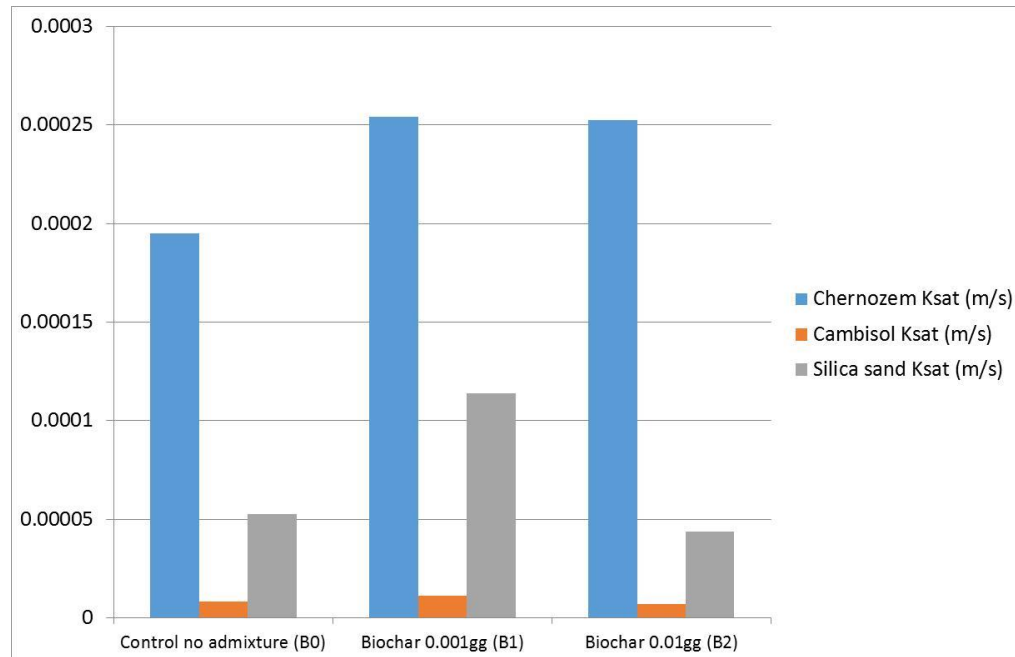


Figure 15. Average hydraulic conductivities over all replications

5.3. Soil water retention curves

As the retention curves were only measured for the silica sand, the resulting data are limited. The curves are presented graphically in Figs. 16 and 17, including minor artefacts at the beginning of the drying, when the HYPROP tensiometers were just about to acquire a hydraulic contact with the soil. Moreover, Table 8 shows water content at three typical matric head values, corresponding to standard soil water states, namely, the matrix saturation ($h = 10$ cm), the field capacity ($h = 330$ cm) and the wilting point ($h = 15000$ cm).

Table 8. Average water contents of silica sand at typical matric heads h (cm)

Method:		HYPROP		MPS-2	
Matric head (cm):		10	330	330	15000
Biochar concentration (g/g)	0	0.458	0.101	0.022	0.006
	0.001	0.400	0.048	0.019	0.005
	0.01	0.416	0.059	0.056	0.036

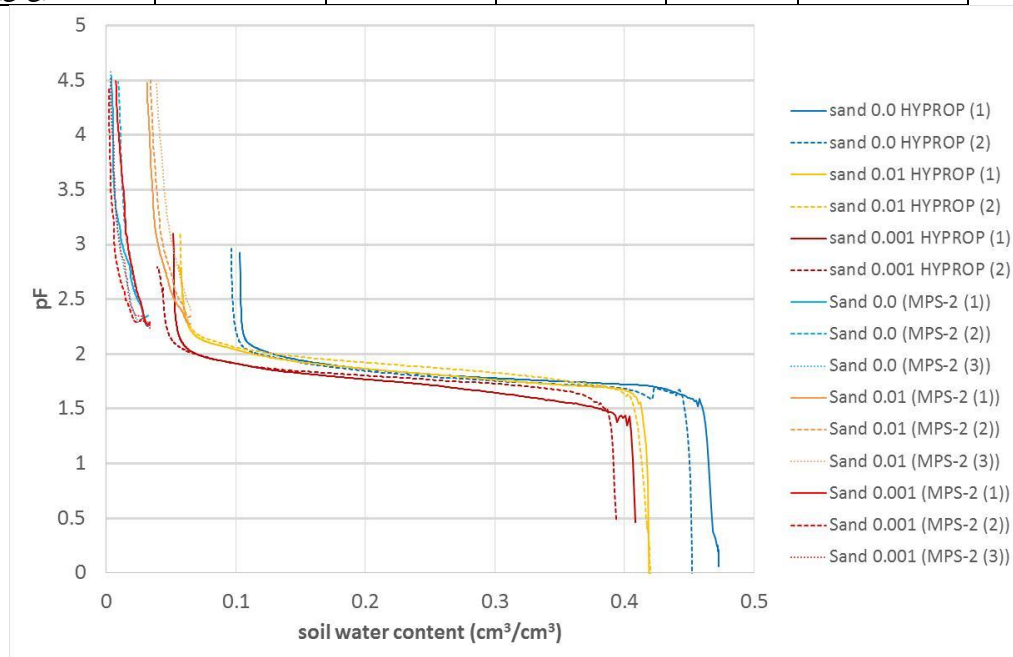


Figure 16. Comparison of water retention carried out on sand with different concentration of biochar – the whole range measured with HYPROP and MPS-2, with a logarithmic vertical scale, $pF = \log_{10}(h(\text{cm}))$.

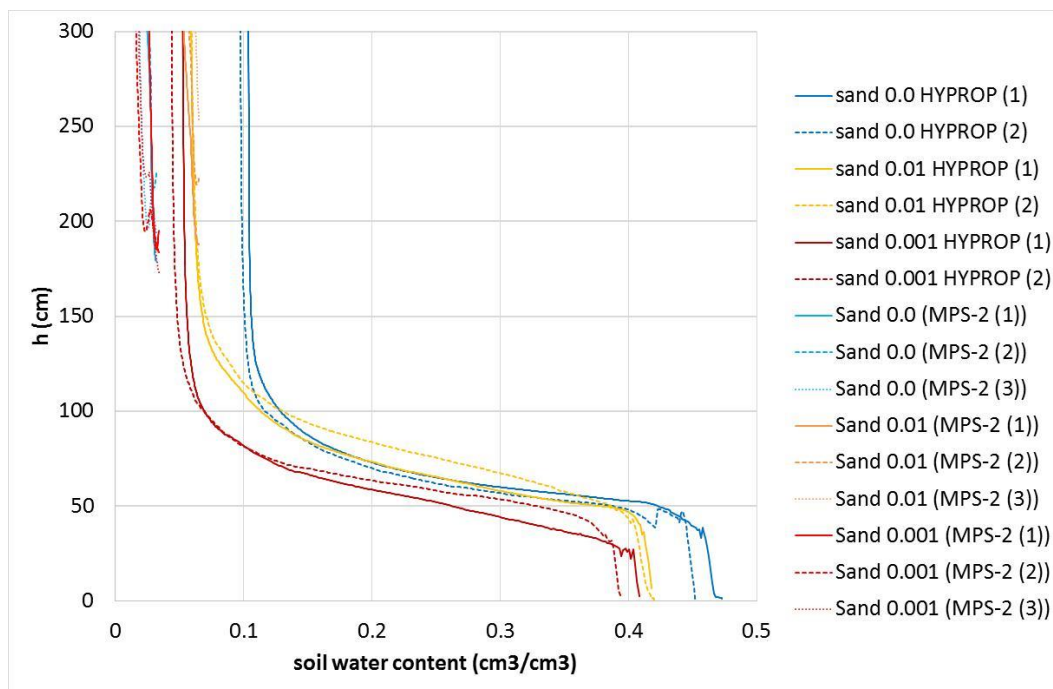


Figure 17. Comparison of water retention carried out on sand with different concentration of biochar – the moist range, measured mainly with HYPROP and only marginally by MPS-2, with a linear vertical scale.

6. Discussion

6.1. Sorptivity

As the variability of the results is high, it was not possible to meaningfully use statistical test. Instead, only arithmetic averages of two parallel measurements for each soil, liquid and biochar concentration were calculated and plotted in graphical form, in order to demonstrate qualitative trends. Figs. 8 to 13 show the following:

- a) The silica sand sorptivities are by about an order of magnitude higher than those of Cambisol and Chernozem, which is expectable with regard to their texture and the permeability of their matrix (without macropores).
- b) Ethanol infiltration runs give lower sorptivity than water runs for silica sand (Fig. 13) but higher sorptivity for Cambisol (Fig. 11) and Chernozem (Fig. 12). This suggests that silica sand is not repellent but Cambisol and Chernozem are. The lower ethanol sorptivity (compared to its water sorptivity) is partly due to higher dynamic viscosity of ethanol (Lamparter et al., 2010).
- c) The effect of biochar is masked by the data noise. It seems (but it cannot be proved with the data at hand), that the addition of biochar reduces the sorptivity of ethanol in Cambisol in the entire range of biochar concentrations, of the silica sand between 0 and 0.001 g/g and of Chernozem between 0.001 and 0.01 g/g. The reduction of water sorptivity is only visible in the range between 0 and 0.001 g/g (except for Cambisol). In any case, the decreasing trend of sorptivity with the increase of biochar concentration is much more pronounced than the opposite trend.
- d) The use of tension infiltrometer for the testing of influence of biochar on the soil's hydrophobicity has not provided us with definite conclusions, which may suggest that a different, more sensitive technique should be looked for.

6.2. Saturated hydraulic conductivity

It follows from Table 7 and Figs. 14 and 15 that there obvious and significant differences in the saturated hydraulic conductivity between different soils. Chernozem is by far the most conductive, and this is due to its numerous macropores – large inter-aggregate pores. When this result is compared with the results of sorptivity, which characterizes the effect of matrix without large macropores, we see how important the macropores and aggregates are. The second in terms of hydraulic conductivity is the silica sand, while Cambisol is the least conductive.

The effect of biochar addition is less obvious. It is by no means negligible, but the effect seems to be largest for the low doses of biochar (0.001 g/g). This is valid for the silica sand as well as for Cambisol. The hydraulic conductivity of Chernozem remains raised even at 0.01 g/g.

6.3. Soil water retention curves

Discussion to the HYPROP method

The matric potential of the soil is measured in two depths within the core sample. Their values slightly differ, especially when the sample gets drier. An average of the two values should be used for soil water retention curve construction. In this thesis, only the data from the top tensiometers (the longer ones) were used, because the bottom tensiometers (the shorter ones) were affected by cavitation at much lower tension. The shorter tensiometers are more sensitive to cavitation due to their smaller inner volume. Degassing of the microtensiometers' ceramic tips is the most critical part of the measurement.

Discussion to the MPS-2 method

The samples showed very little change of pressure head at the beginning of the evaporation experiments, while the water content was decreasing with almost linear trend. During the third or fourth day of measurement, the pressure head (its absolute value) started to increase significantly. There is a presumption, that only at this time the sensors get a good hydraulic contact with the sand and their water starts be in equilibrium with the water in the surrounding soil. Based on it, only those parts of the curves were further used for evaluation.

Although the experiments were prepared carefully, the initial state of the soil at each biochar concentration level was different (see Tab. 5) and the variability of the initial soil water content and the dry bulk density values of the soil was rather high. No standard procedure exists for this type of measurement and the experimental setup is a compromise between the availability equipment and a rather low weighing capacity of the scales used (max. 810 g). However, the results provided valuable information for any following measurements.

Discussion to results

The influence of biochar addition on the silica sand retention is not entirely definite. The noise, cause by uncertainty in the dry bulk density of the soil, overshadows to some extent the effect of biochar. The increase in soil water retention capacity due to biochar is clearly perceivable between 0.001 and 0.01 g/g biochar concentration and this applies to all matric heads, while the sand without biochar appears to have the highest retention capacity, except at the wilting point.

7. Conclusions

Altogether, we can say that the effect of biochar addition on the soil physical properties is clearly perceivable but not as strong as one might expect based on some optimistic reports in the literature (see the review of literature for details). However, even the existing literature indicates that this effect is small or none in some cases.

This thesis was based on the model of loose soil after cultivation, where the effect was supposed to be the largest. On the other hand, for a loose soil it is difficult to maintain its dry bulk density reproducibly constant. The future research in this direction must pay more attention to the control of dry bulk density.

The identified effects of biochar addition are the decrease in sorptivity, the increase in saturated hydraulic conductivity and the increase in the water retention capacity. However, these effects are not obvious and are not always observed. This would probably happen with the higher doses of biochar above the economic limits.

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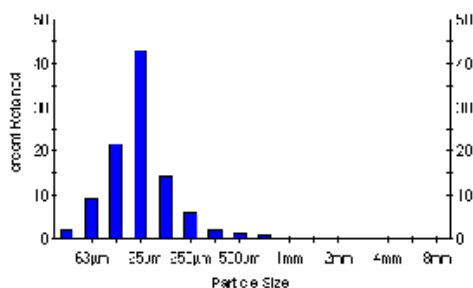
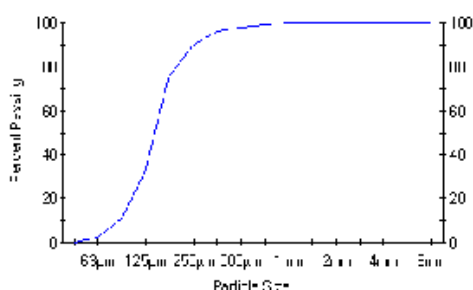
Appendices

Appendix A. Properties of the fine silica sand, ST 56, after laboratory analysis of samples (Sklopisek Střeleč, a.s., 2015. available at <http://www.glassand.eu/GB/pisky/ST56Sporttop.pdf>)



ST 56 *SportTop* – Sand for Sport Surfaces

ST 56 *SportTop* is useful for equestrian use as it is predominately fine and very fine sand. Therefore giving suitable stability for this application.



Category	Diameter (mm)	% Retained
Stones	>8	0.0
Coarse Gravel	8 - 4	0.0
Fine Gravel	4 - 2	0.0
Very Coarse Sand	2 - 1	0.0
Coarse Sand	1.0 - 0.5	2.1
Medium Sand	0.5 - 0.25	8.0
Fine Sand	0.25 - 0.125	56.9
Very Fine Sand	0.125 - 0.063	30.8
Silt/Clay	<0.063	2.2

Microns	% Passing	% Retained
8000	100.0	0.0
5600	100.0	0.0
4000	100.0	0.0
2800	100.0	0.0
2000	100.0	0.0
1400	100.0	0.0
1000	100.0	0.0
710	99.9	1.0
500	97.9	1.1
355	95.9	2.0
250	89.9	6.0
180	75.8	14.1
125	33.0	42.8
90	11.3	21.7
63	2.2	9.1
Pan	0.0	2.2

150 µm % Passing	54.9
125-150 µm % Retained	21.9
150-250 µm % Retained	35.0

D Values	
D0 (µm)	-
D5 (µm)	71
D10 (µm)	85
D15 (µm)	96
D20 (µm)	105
D50 (µm)	143
D60 (µm)	155
D85 (µm)	209
D90 (µm)	251
D95 (µm)	326
D100 (µm)	986
D90/D10	2.9

D eff (µm)	109
Total Porosity (%)	37.3
Percolation (mm/h)	143
Critical Tension (mm)	657

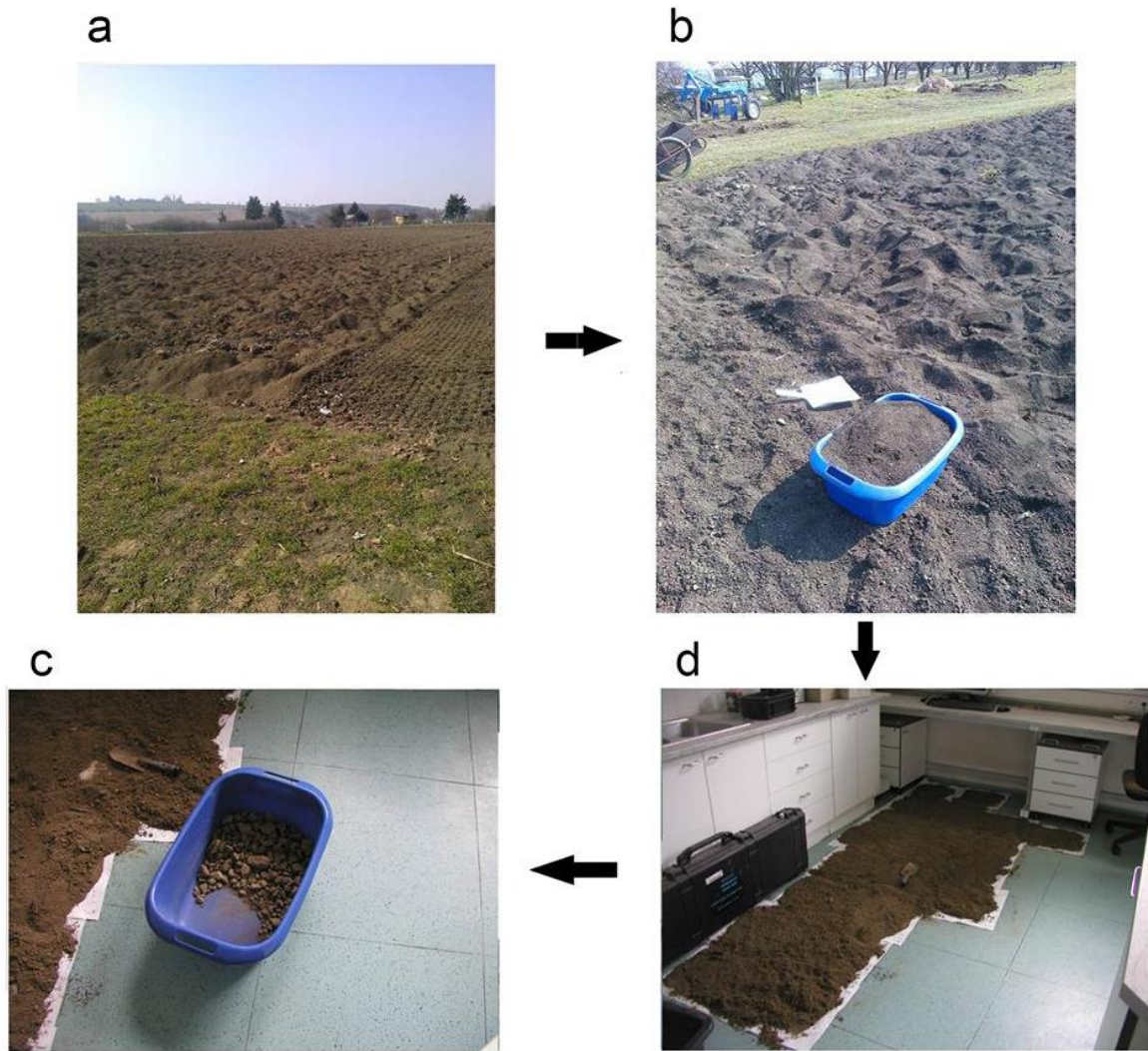


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Appendix B. Collection of Cambisol soil from the top 0-20 cm depth from the experimental field of the Potato Research Institute Havlíčkův Brod, Ltd., research station Valečov, and then put them into a large container (a, b and c). Then air dried, sorted and separating of the gravels from soils were made (d) and then sieved with 5mm (e) and weight them after homogenization by coning and quartering method (f, g and h) and we took four samples to measure the water content of the soils (f) before we put the soils into the plastic bag ready for subsequent experiments (i).



Appendix C. Collection of Chernozem soil from the experimental field of CULS, Suchdol, Prague in the same processes described in Appendix B. The fine silica Sand with the commercial name ST 56, also undergo the same process as in Appendix B even though it is more uniform and homogenous (Appendix A) than CH and CM.



Appendix D. Dimension of the ceramic dishes used for the mini disk experiments. Top upper exterior and interior diameter of 23.6 cm and 22.2 cm respectively, inside bottom inner diameter of 18.5 cm, height of 4.5 cm (a and b). Filter paper put at the bottom of the dish for a capillary rise of the tap water (c) and a 100 cm³ sampling ring at one side of the dish before filling the dishes with soil up to 1.5 cm below of the upper edge of the dishes (d).

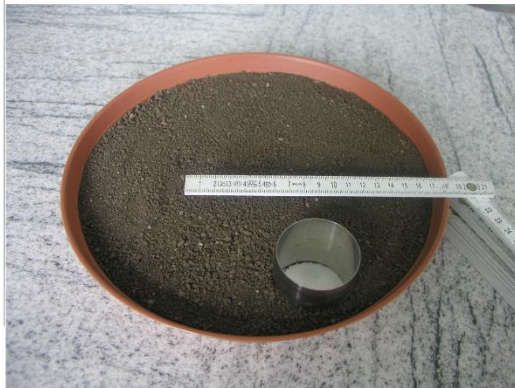
a.)



b.)



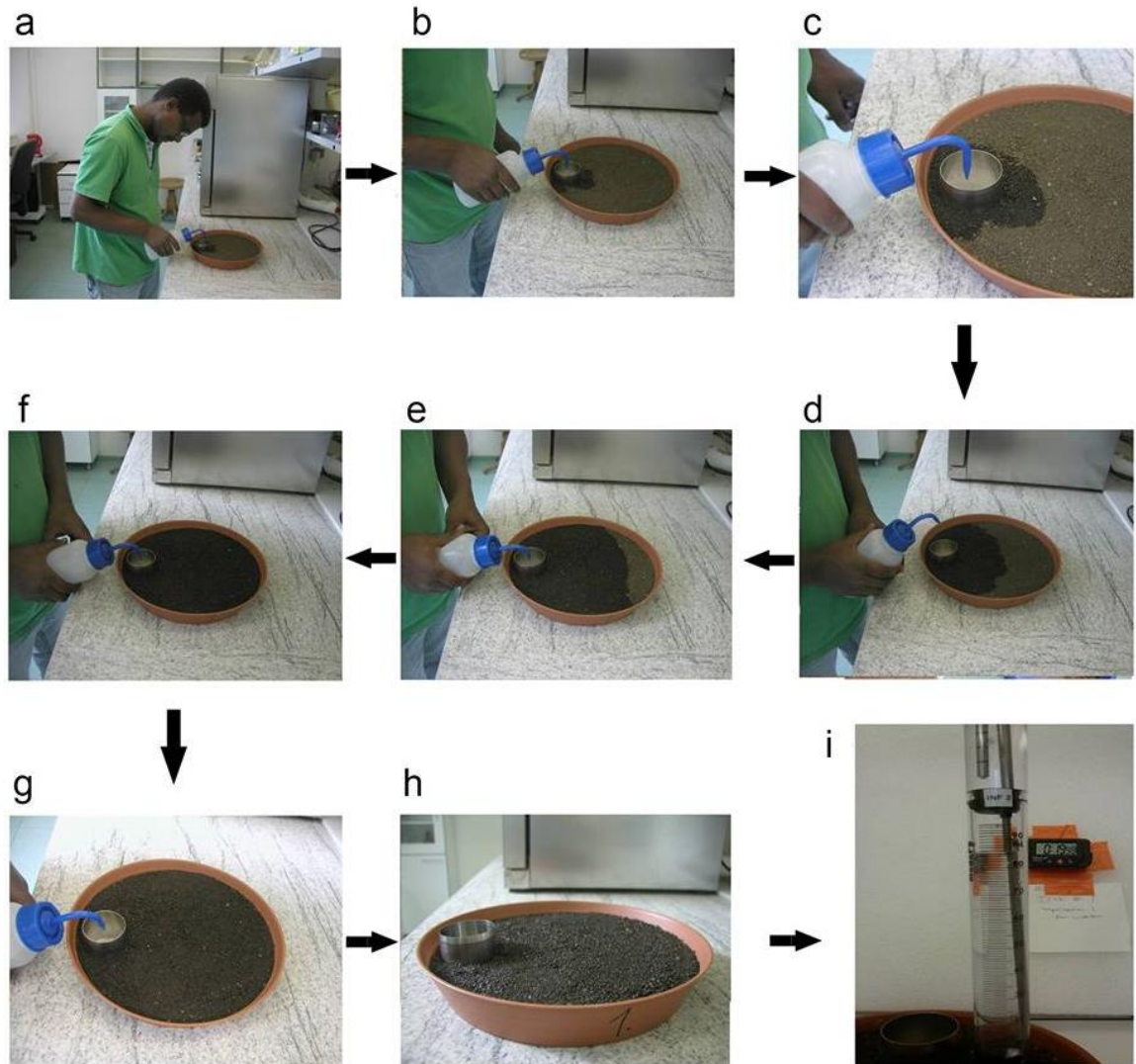
d.)



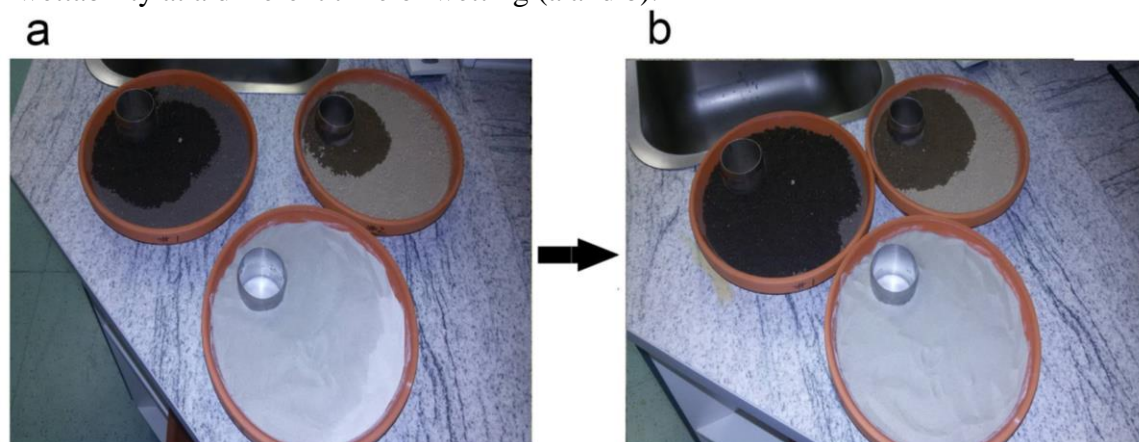
c.)



Appendix E. Wetting a soil by putting a thin layer of water, about 2 mm, slowly about 1mm height into a filter paper at the bottom of the dish using a pipette. The water layer were arisen in the basal filter paper and in the bottom about 1 mm of the soil to enable the capillary rise of water into the entire thickness of the soil in the dish.



Appendix F. Comparison of the three soils: Chernozem [the darker colour, due to high organic matter content around 3.47 (*Kodesova, 2011*)], Cambisol (gray) and fine sand (white in color), in their wettability at a different time of wetting (a and b).



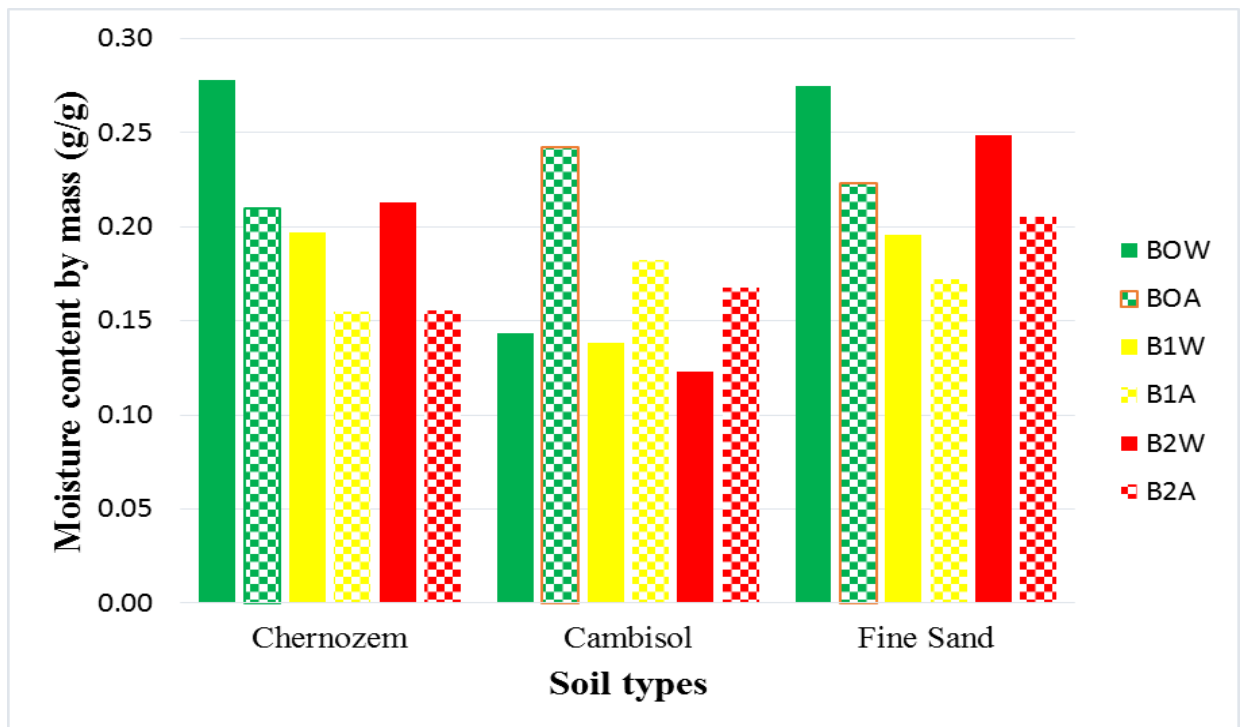
Appendix G. Amount of water added to the ceramic dishes and duration of wetting for the three soils.

Soil types in ceramic dish	Amount water added to the dish with soils for wetting (in ml)	Duration of wetting (in min)	at 24.6 °C
Chernozem	291.30	112	
Cambisol	344.60	242	
Fine Sand	344.00	42	

* Even if the fine sand wetted by capillary rise very quickly than the others two soils as can be seen also from appendix F, this doesn't show the water holding capacity of the soils at the same time, there is evaporation (24.6 °C) especially for Cambisol which takes long time relatively for wetting.

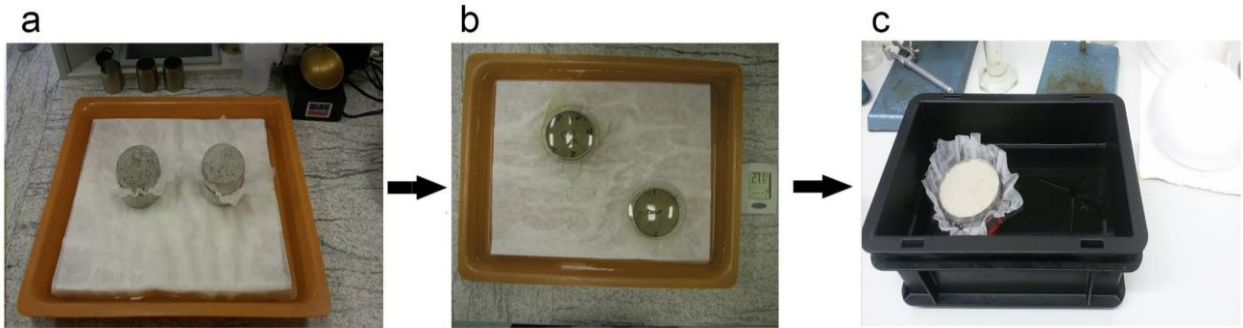
Appendix H. Moisture content of by mass (g/g) of soils after mini disk experiments. Except in the case of Cambisol, the water content by mass of Chernozem and fine Sand higher than the alcohol content by mass.

The ratio of the final water content to the final alcohol content should be roughly equal to the ratio of water density to alcohol density. This is true for Chernozem and sand but not for Cambisol, which clearly indicates hydrophobicity of Cambisol.

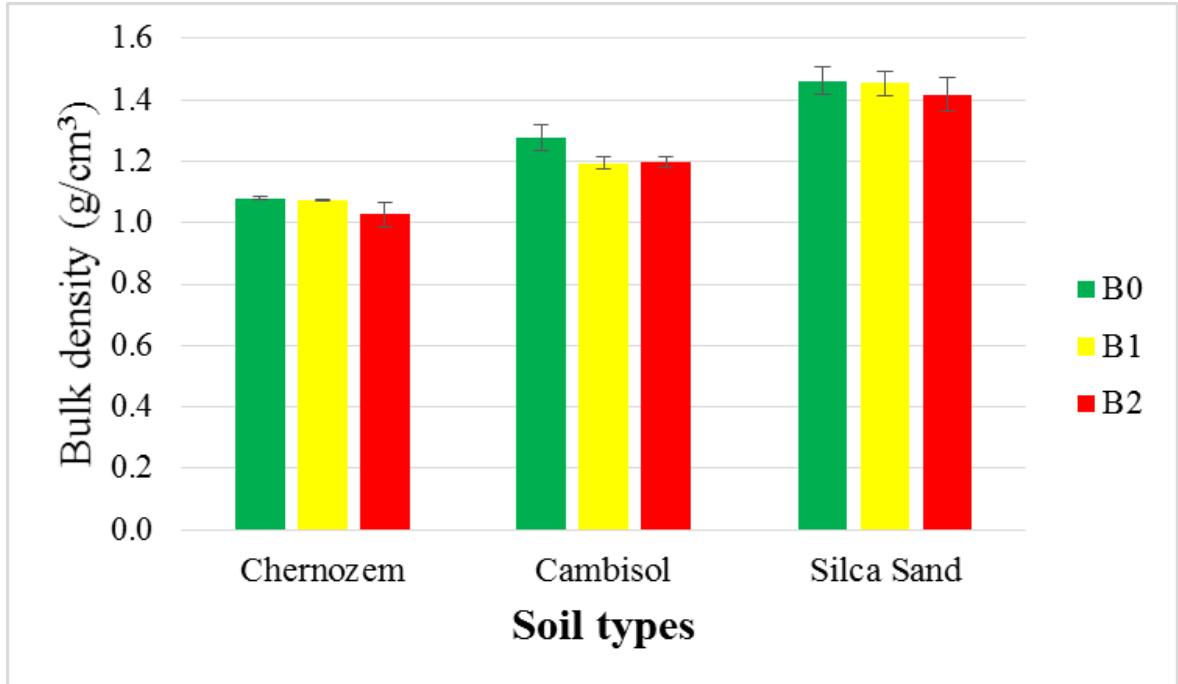


Keys. BOW – control (without admixture), experiment with water
 BOA – control (without admixture), experiment with alcohol
 B1W – soils with 0.001g/g biochar, experiment with water
 B1A – soils 0.001g/g biochar, experiment with alcohol
 B2W – soils 0.01g/g biochar, experiment with water
 B2A – soils 0.01g/g biochar, experiment with alcohol

Appendix I. Saturation of soil samples in a saturation mat for 12 hours (a and b), covering the top part of the ring to avoid evaporation for Ksat and Hyprop experiments (b). Before the Ksat experiments, additional wetting for 10 minutes were made in a rectangular pot filled with water till 2 cm below the 250 cm³ ring (c).



Appendix J. Average bulk density (g/cm³) of soil samples with different concentration biochar (B0, B1 and B2) for samples prepared for Ksat and HYPROP measurements. The graph shows biochar tends to decrease the bulk density.



Keys: B0 – soils control (without admixture),
 B1 – soils with 0.001g/g biochar,
 B2 – soils 0.01g/g biochar,

Appendix K. Preparation of soil samples for Hyprop experiments after saturation is made overnight as shown in Appendix I (a and b).

