Biochar in soil: Effect on physical, chemical and hydrological properties in differently textured soils.

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Biochar in soil: Effect on physical, chemical and hydrological properties in differently textured soils

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Cover illustration: Repacked biochar soil mixtures in the sandbox for determination of physical soil properties, by Ann-Kathrin Teβin

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**Preface**

This thesis is the termination of my MSc programme in agro environmental management at Aarhus University. The experimental work was carried out at the department of Agroecology, Aarhus University, in Foulum from September 2015 to August 2016.

The aim of the study was to evaluate the effect of biochars derived from different feedstocks under different production temperatures, on important soil properties.

This thesis is divided into chapters, containing an introduction, materials and methods, results with discussion, and a short sub- conclusion. The main conclusion and future perspectives are formulated in the very end.

**Acknowledgements**

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And last but not least a genuine thanks to all people in my personal life, with a special thanks to my boyfriend Marc, who was incredibly supportive and did a great job in helping me keeping my head up and making me laugh.

_________________________________________

Ann-Kathrin Teßin,  
August 2016
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<tr>
<td>LUN</td>
<td>Sandy soil from Lundgaard</td>
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<tr>
<td>ASK</td>
<td>Sandy loam soil from Askov</td>
</tr>
<tr>
<td>STEN</td>
<td>Clayey soil from Sdr.Stenderup</td>
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<tr>
<td>JYN</td>
<td>Coarse- grained sandy soil from Jyndevad</td>
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<td>SWP 7</td>
<td>Softwood biochar produced at 700°C</td>
</tr>
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<td>OSR 7</td>
<td>Oil seed rape biochar produced at 700°C</td>
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<tr>
<td>NIMA</td>
<td>Biochar derived from straw produced at 750°C</td>
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<td>$K_{sat}$</td>
<td>Saturated hydraulic conductivity (cm/hour)</td>
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<tr>
<td>$K_a$</td>
<td>Gas transport parameter (air permeability)</td>
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<tr>
<td>$D_p/D_o$</td>
<td>Gas transport parameter (gas diffusivity)</td>
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<td>Soil water retention curve</td>
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<td>pF</td>
<td>Suction (Matric potential)</td>
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<tr>
<td>EC</td>
<td>Electrical conductivity</td>
</tr>
<tr>
<td>DOC</td>
<td>Dissolved organic carbon</td>
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<td>P</td>
<td>Phosphorus</td>
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Abstract
Biochar is a stable, carbon rich product obtained by the thermal degradation (pyrolysis) of biomass. Biochar exhibits a highly porous structure and a large reactive surface area that differs depending on the feedstock used and the process temperature. The use of biochar for agricultural purposes is suggested to improve a range of soil properties, including a liming effect, water holding capacity and nutrient retention.

The aim of this study was to investigate the effect of biochar, derived from different feedstocks, in increasing concentrations on physical, chemical and hydrological properties in different textured soils (sandy, sandy loam, clayey).

For the physical and chemical characterization of biochars and soils, different experimental setups were conducted. The specific surface areas were determined with the EGME method, the bulk density, total porosity and air filled porosity of pure soils and soil biochar mixtures in the concentrations 0.5, 1 and 2 % were determined in 100 cm³ steel rings. Additionally, the soil water retention capacity from matric potential, pF 1 to pF 3 was investigated in the laboratory using tension- and pressure plates. At matric potentials (pF 1.5, 2 & 2.7) the gas phase parameters (air permeability (kₐ) and gas diffusivity (Dₚ/Dₒ)) were measured. The saturated hydraulic conductivity was measured with the “constant head method”.

The pH, electrical conductivity (EC) and the potential release of dissolved organic carbon (DOC), and phosphorus (P) was determined in pure soils, biochars and in soil biochar mixtures with a batch extraction experiment. A column leaching experiment on columns with and without application of straw biochar in coarse-grained sandy soil was conducted to quantify the release of colloids, DOC and P. Changes in the percolation pattern in the reference and biochar amended soil columns were found by adding a neutral tracer (tritium) for characterization of water transport through soils to the columns. In addition to the column leaching experiment, a lysimeter leaching experiment, located in Askov (Southern Jutland), with differently textured soils and increasing biochar application (0, 0.5, 1, 2 %), was implemented into this study, to examine the release of colloids, DOC and P in the effluents.

The chemical and physical characteristics of the eleven biochars (wood and straw-based) were found as widely different, depending on the feedstock and the process temperature used. The biochars produced at 550°C had a larger specific surface area, a lower pH and electric conductivity and a higher potential release of dissolved organic carbon compared to the biochars produced at 700°C. The findings of the batch experiment determined that the application of 2% of the alkaline biochars to four different textured soils (sandy to clayey) increased the pH, but will have a minor influence on the EC and the potential release of DOC.
and P, revealing that it is more likely the soil type governing these properties. In the sandy soil, the biochar induced increase in pH increased the release of DOC and P.

The highest water retention capacities were observed at 2 % application (biochar derived from soft wood, oil seed rape and straw). The same biochars decreased the saturated hydraulic conductivity in the sandy soil with up to 56 % compared to the reference. The gas transport parameters (air permeability $k_a$ and gas diffusivity $D_p/D_0$) were positively related with the air filled porosity.

The shape of the tritium breakthrough curves for the reference soil (sandy) and the biochar amended soil, and the significantly lower peak concentration in the biochar amended soil, affirmed that the transport of water and solutes through the soil matrix will be positively altered when biochar is used as a soil amendment.
Sammendrag (Danish summary)

Biochar (biokoks) er et stabilt, kulstofholdigt produkt der opstår ved termisk nedbrydelse (også kaldt for pyrolyse) af biomasse. Biochar har en særdeles porøs struktur og et meget stort, reaktivt overfladeareal, som varierer alt efter hvilken biomasse der anvendes og ved hvilken temperatur, processen foregår. På baggrund af de fordelagtige fysiske og kemiske egenskaber er brugen af biochar i landbruget blevet foreslået for at forbedre en række egenskaber i jorden, heriblandt kalkning af jorde med lav pH, evnen til at holde på vand og tilbageholdelsen af næringsstoffer.

Formålet med denne afhandling var at undersøge effekten af biochar stammende fra forskellige råstoffer, som er blevet iblandet forskellige jordtyper i varierende koncentrationer, på fysiske, kemiske og hydrologiske egenskaber.

Der blev udført adskillige eksperimenter for at bestemme de fysiske og kemiske egenskaber af biochar og jorde. De specifikke overfladearealer blev bestemt ved hjælp af EGME metoden, endvidere blev volumenvægten, den totale porositet og den luftfyldte porositet af de rene jorde, biochars og jord-biocharblandingerne i koncentrationerne 0,5, 1 og 2 % bestemt i 100 cm³ stårlinge. Desuden blev der i laboratoriet, ved hjælp af sandbokse og trykgryder, målt vandretentionen på jordprøverne ved forskellige vandpotentialer. Ved vandpotentialerne (pF 1,5, 2 og 2,7) blev gastransportparametrene, luftpermeabilitet og ilddiffusion, målt. Den mættede hydrauliske ledningsevne for jordprøverne blev fundet ved hjælp af "constant head "-metoden.

pH-værdien, den elektriske ledningsevne (EL) og den potentielle frigivelse af opløst organisk kulstof og fosfor blev bestemt i rene jorde, biochars og jord-biocharblandingerne ved anvendelse af et portionekstraktionsforsøg. Et kolonneudvaskningforsøg på kolonner med og uden tilført biochar i grovsandet jord blev udført for at kvantificere de undslupne kolloider, DOC og P. Der blev tilført et neutralt sporestof for at kunne identificere, om biochar har potentielle til at forandre gennemløbet af vand. Herudover blev effekten af den samme biochar (som i kolonneforsøget), i koncentrationerne 0, 0,5, 1 og 2 %, på udvaskningen af kolloider, DOC og P målt i tre forskellige jordtyper i et udendørslysimeterforsøg beliggende i Askov (Syddanmark).

De kemiske og fysiske egenskaber af de 11 biochars (træ- og stråbaseret) blev konkluderet til at være forskellige alt efter hvilken råstof og temperatur, der blev brugt ved fremstillingen. Biochar produceret ved lavere temperatur (550°C) havde et større, specifikt overfladeareal, en lavere pH og EL og et højere potentielle at frigive opløst organisk kulstof end biochar fremstillet ved højere temperatur (700°C). Resultaterne af portionekstraktionsforsøget viste, at påføringen af 2 % basisk biochar på fire forskellige jordtyper (fra sandet til lerholdigt)

Den højeste vandretention blev observeret ved påføringen af 2 % biochar (træ, raps og strå). Den samme biochar mindskede den mættede hydrauliske ledningsevne i den sandede jord med op til 56 % sammenlignet med referencen. Gastransportparametrene (luftpermeabilitet og iltdiffusion) steg i takt med højere luffyldt porøsitet.

Der kunne ses en signifikant lavere maksimumskoncentration af tritium i den biochar påførte jord. Dette tyder på en ændring af transporten af vand og opløst stof igennem jorden.
1 Introduction
The growing population and consequential demand for food is an ongoing challenge the world is facing (Godfray et al., 2010). From an agricultural perspective, the term ‘food security’ implies an urgent necessity to safeguard one of the world’s most valuable resources, namely the soil. The FAO (Food and Agricultural Organization of the United Nations), stated in “The State of the World's Land and Water Resources for Food and Agriculture”, that agricultural land productivity has doubled in the last 50 years (FAO, 2011). However, according Blanco and Lal (2008), about one-third of the world’s soils are experiencing a decrease or total loss in productivity since 1970.

Soil is the organic and inorganic material on the very surface of the Earth a thin layer of fragmented rocks and decomposed organic material (Whalen and Sampedro, 2010) originating from physical and chemical rock weathering (Loll and Moldrup, 2000). The soil provides the entire biosphere with a wide variety of ecosystem services. For example, the soil provides a habitat for a diversity of soil organisms and animals, supporting plant growth, acting as a medium for plant roots and supplies essential nutrients and water to plants (Brady, 2010). Moreover, the soil plays an important role in the regulation of the natural cycles of water, air, carbon and nitrogen, contributing to the reduction of global warming, due to gas exchange processes between the atmosphere and the soil. The soil can also provide clean drinking water because it has the ability to filter organic substances, and heavy metals or pesticides that have been added to fields, gardens, etc., preventing such pollutants to end up in the groundwater (Blume et al., 2009).

One of the most important functions of the soil is for agricultural production, where the soil represents a fundamental component for human-and animal life, providing the entire civilization with food (Whalen and Sampedro, 2010). Soil degradation is an ongoing global problem, with approximately 33% of the Earth’s land surface currently affected by some kind of soil degradation (Lal, 2015). However, the soil is nonrenewable over a lifetime. Soil degradation includes a decrease in soil quality, and is a threat to all living organisms. Therefore, the awareness and understanding of fundamental processes in the soil are of great importance for us, as humans, to prevent soil degradation and possibly even improve the soils that have already been affected by degradation.

The soil is a heterogeneous three-phase system, where different size minerals and decomposed organic material represents the solid phase. The pore space between the solid material is filled with soil water and air (Loll and Moldrup, 2000). The soil particles in the solid phase are formed of rocks (parent material) by physical and chemical processes, such as thermal phenomena, which is the grinding of particles moved by water, hydration, oxidation,
chemical exchange reactions, etc. The soil particles are separated based on their size, and traditionally divided into three overall size ranges, clay (<2 µm), silt (2-50 µm) and sand (50-2000 µm).

The soil organic matter fraction originates from partially decomposed plant and animal residue that is continually broken down by soil organisms, but is also easily renewed by the addition of new residues. The organic matter molecules can be compared to the size of clay minerals (<2 µm) and is often specified as humus. Soils are classified into textural classes according to the content of clay, silt and sand in the soil (Loll and Moldrup, 2000).

The soil structure is the spatial arrangement of the soil solids. Soil particles can be found in almost complete dispersion or the minerals and the organic material are present as soil aggregates. In the soil aggregates, the organic material is responsible for the formation and stabilization of the aggregates (Loll and Moldrup, 2000).

Fertile soil with an ideal condition for plant growth, consists of approximately 50% solid minerals of different shapes and sizes, with organic material only accounting for about 5%, and 50% water and air (Figure 1). The water and air in the soil is located in the pore spaces between the solid materials, where the proportion of the two will fluctuate as water is added or lost (Brady, 2010).

The proportion of the different components may vary depending on type of soil, saturation, compactness, etc. The interrelationship between soil texture, soil structure and the pore spaces between the solid materials is referred to as the soil matrix. In the matrix processes of water- and heat balance and various chemical and biological processes takes place, but also washouts and accumulations take place. To evaluate these processes, further physical characteristics are important, such as the bulk density (mass of a unit volume of dry soil, both solids and pores) (Brady, 2010).

1.1 Soils as a filter
The soil acts as a filter for nutrients and pollutants, the filtering effect is an important ecosystem service and differs from soil to soils (Schaik et al., 2012). The texture of the soil has a strong influence on soil productivity and the role soil has as a filter for nutrients and contaminants entering the soil. When the particle size decreases, the specific surface area...
per unit mass of material increases. For example, small clay particles are negatively charged, due to crystalline structures, and have a very large surface area (5-800 m² g⁻¹) (Loll and Moldrup, 2000). Large sand and silt particles are neutrally charged and have a low surface area (around 0.04 to 1.1 m² g⁻¹). Since soil is an electrical system, it will work as a filter, where minerals with negatively charged surface areas, such as clay minerals (cation exchanger), are very reactive and can adsorb big amounts of positively charged, organic and inorganic substances. The particularly reactive colloidal fraction, fine clay particles and humus, have a large influence on soil behavior, as they protect nutrients, such as phosphorus, from leaching, and increase the water holding capacity in the soil (Blume et al., 2009).

Fine textured soils are therefore distinguished water reservoirs, adsorbing nutrients and contaminants, whereas soils with high sand fractions are often not capable of storing enough water for plant supply, and nutrients and contaminants are easily transported into the groundwater (Brady, 2010).

Most exchange processes (adsorption and desorption) will appear at the interface between the soil matrix and the soil water. In the soil water, decomposition products from plant and microbial biomass will be present as dissolved organic matter (DOM) / dissolved organic carbon (DOC). The DOM in soils can have an important role in the transport of pollutants in soils (Kalbitz et al., 2000).

Fine textured soils are therefore, based on their reactive particle fraction, and the good water holding capacity, suitable sites for an efficient crop production. However, currently one of the main concerns is the lack of these applicable sites for agricultural production, since many agricultural soils do not have the capability to adsorb contaminants and nutrients. These soils are often sandy soils with a low organic material content, and hence a low water holding capacity, resulting in fast leaching of contaminants and nutrients into the groundwater (Brady, 2010).

Since healthy soil equals healthy food supply, it becomes even more important to promote and ensure the productivity of the remaining agricultural sites. Additionally, the productiveness of low yielding sites needs to be enhanced. Therefore, many studies conducted concentrate on the issue of soil conversation and improvement of soil function using charred biomass substrates, called biochar.
2 Biochar in soil

Biochar is a carbon rich product that is obtained by the burning of biomass in the absence of oxygen (pyrolysis), where a part of the biomass is transformed into gaseous and liquid compounds. The biochar remains as a concrete mass of stable carbon (Lehmann and Joseph, 2009).

Biochar incorporated into soil is believed to improve a range of soil functions important for plant growth. Since biochar cannot be removed again once incorporated into the soil, it is very important to investigate the complete list of pros and cons biochar might trigger in the soil before it is applied. However, the pyrolysis process can result in different fundamental biochar materials with different properties and therefore they do not have the same effects on the soil.

2.1 Biochar Production

The artificial production of biochar generally applies two methods, pyrolysis and hydrothermal carbonization. In both charring processes, organic biomass substrates (feedstock, manure, straw, etc.) are converted to carbon rich products, due to thermochemical processes under limited or no available oxygen supply (Lehmann and Joseph, 2009). Different biomass contains different fractions of fixed carbon and different amounts of lignin, cellulose and other organic compounds that will degrade at different rates and respond differently to temperatures (Bridgwater, 2012).

For the pyrolysis process, there are different operating modes, including fast, intermediate and slow pyrolysis and gasification. The starting material for all modes of pyrolysis has to be dried (less than 10% water) before entering the pyrolyser (figure 2), and during pyrolysis three products are always produced, namely gas, liquids and char.

Figure 2. Biochar production, where biomass is heated with little or no oxygen (pyrolysis) The process produce clean energy (gas and oil) and biochar, (from Initiative (2016))
Figure 3 illustrates two different kinds of feedstock (rice husk and straw) used for the production of biochar.

![Image](image1.png)

Figure 3. (Left) biochar derived from rice husk, (right) biochar derived from straw.

Generally, the slow pyrolysis with low process temperatures (~400°C) and long vapor residence times (hours-days) are resulting in high yields of charcoal (approximately 35%). The intermediate and fast pyrolysis with moderate temperatures (~500-700°C) and short vapor residence time (1 to 30 sec.) favors the production of liquids (50-75%). Biochar yields and volatile contents will decrease with increasing treatment temperatures. Therefore, high temperatures (~750-900°C) and longer residence time favor biomass conversion to gas (85%), see figure 4 (Bridgwater, 2012).

![Image](image2.png)

Figure 4. Composition of percentage yield of organics, water, char and gas under four different treatments, from (Bridgwater, 2012).
Several studies have shown that higher treatment temperatures lead to higher surface areas, until temperatures are reached where deformation occurs (Lehmann and Joseph, 2009).

The hydrothermal carbonization treatment takes place in a wet environment, where the biomass is placed in an autoclave under pressure and temperatures ranging from 200-250°C for 2-4 hours. For both the pyrolysis and the hydrothermal carbonization, studies have shown that the original porous structure of the organic biomass broadly will be maintained (Cutter et al., 1980).

2.2 Characteristics and properties of biochar

Depending on the starting material and process parameters (temperature, residence time, etc.), the biochar will obtain different physical and chemical structures that can modify the physical and chemical characteristics of the soil. The biochar product is believed to be resistant to microbial decomposition (Lim et al., 2016). Biochar additions may positively affect the soil carbon (C) sequestration and, thus, act as a sink and long-term storage of C due to its long residence time in the soil ranging from 100 to 1000 years (Verheijen et al., 2010). There is a high variability among the characteristics of different biochars, but in case of pH, biochars are usually alkaline (pH>7) (Lehmann and Joseph, 2009).

2.2.1 Physical properties

The physical characteristics of biochar depends on the biomass used, the pre- and post-handling of biochar, and the type of treatment. It is expected that the maximum treatment temperature is the most important factor for physical changes of the biochar product, followed by the heating rate and pressures (Lehmann and Joseph, 2009).

The biochar structure is amorphous, containing local crystalline structures of joint aromatic compounds (Grabler et al., 2011). The carbon skeleton formed during pyrolysis of organic matter results in a high porosity of biochar, due to its sponge-like structure (Figure 5) (Kumari, 2015). The voids are formed as pores present as macro- (>50µm), meso- (2-50µm) and micropores (<2µm) as seen in figure 5. The large proportions of micropores (<2 x 10⁻⁵µm in diameter) is responsible for the increasing surface area, that can reduce the mobility of soil water (Lehmann and Joseph, 2009). The high porosity results in a low bulk density, which when incorporated to the soil in sufficient concentrations can reduce the total bulk density of the soil (Laird et al., 2010). Most biochar exhibits a large surface area, depending on the base material and treatment. For biochar obtained from pyrolysis, surface areas range from 20 m²g⁻¹ (Chen et al., 2008) up to 3000 m²g⁻¹ (Guo et al., 2002). The large surface area of biochar will increase the ion exchange capacity and the sorption of nutrients (Lehmann and Joseph, 2009). The amount of adsorbed water is directly dependent on the surface area,
therefore biochars are able to adsorb large amounts of water. The process of water adsorption on the surface area of biochar is governed by the functional groups (Antal and Grønli, 2003).

When added to the soil, biochar will increase the total soil surface area, which is one characteristic, that is believed to be responsible to overcome the problem of too much water held in clay soils, due to increased soil aeration, and increase the water content/water holding capacity in sandy soils (Lehmann and Joseph, 2009).

![Figure 5. Close up of biochar demonstrating the highly porous structure (from Lehmann and Joseph (2009)).](image)

The particle size distribution of biochar is highly dependent on the feedstock used. In general, wood-based biochars are coarser and of xylem structure, while biochars obtained from crop residues are finer and of recalcitrant structure (Verheijen et al., 2010).

### 2.2.2 Chemical properties

The chemistry of biochar is highly dependent on the biomass used, temperature during pyrolysis and residence time. However, all biochars are composed of condensed aromatic ring structures that become larger and even more condensed with increasing pyrolysis temperature. Hamer et al. (2004) found that biochars obtained by maize, mineralized more rapidly than wood biochar and concluded this to be due to wood biochar having greater aromatic carbon content. Studies on the effect of pyrolysis temperature on biochar chemistry found that faster mineralization occurred in biochars produced at 400°C than in biochars produced at 550°C (Singh et al., 2012).

It is known that a range of functional groups exist on the surface of biochar, such as heteroatoms (hydrogen, oxygen, nitrate, phosphorus and sulfur), acidic carboxyl groups and other basic functional groups (chromenes and pyrenes) (Lehmann and Joseph, 2009). However, the presence of functional groups on the surface of biochar depends on the type of
feedstock. Moreover, the overall assumption is that temperatures above 600°C will decompose the functional groups through heat degradation (Jindo et al., 2014).

Most biochars have a strong surface area charge and thereby a high cation exchange capacity (CEC) having both cation and anion exchange capacity (Gai et al., 2014). Mukherjee et al. (2011) stated that the surface properties of biochar lead to its potentially useful properties, such as contaminant control and the release and retention of nutrients. There is small variability for the pH between biochars, with typical values above seven (Verheijen et al., 2010). The pH and electrical conductivity (EC) for biochars has been found to be higher with higher temperatures. Gundale and DeLuca (2006) concluded that the higher pH with higher pyrolysis temperatures might occur due to the accumulation of oxides of alkaline metals. The high pH of biochar will have a liming capacity, when incorporated into the soil (Chintala et al., 2014).

2.3 Micro- and macronutrients in biochar

The micro- and macronutrient composition of biochar depends upon the nature of the feedstock used and the treatment conditions. As for example will biochars produced from feedstocks with high initial potassium content (animal litters) also have greater potassium content in the biochar product compared to biochar made of wood residues (high carbon content) (Initiative, 2016). The high variability of parameters, including carbon (C), and phosphorus (P) for different feedstock biochars have been found to range between 172 to 905 g kg\(^{-1}\), and 2.7 to 480 g kg\(^{-1}\), respectively (Lehmann and Joseph, 2009).

Liu et al. (2015) found that the C content was significantly higher in biochars produced at high temperatures compared to the same biochar produced at low temperatures (due to a release of hydrogen, resulting in an enhancement of C. Moreover, the C content is dependent on the feedstock used. The study observed lower C contents in manure-based biochars, compared to agricultural residue-based biochars, and concluded this to be due to the greater mass of minerals in manure. The stable form of C in biochars is suggested to be resistant to oxidation and therefore inhibiting the formation of CO\(_2\), decreasing the release of CO\(_2\) (Liu et al., 2015).

2.4 Prospects and concerns of biochar in soil

In recent years the interest in biochar application to soils, with the aim to improve soils and sequester carbon has increased. The number of different experimental set ups with different soil types and biochars (different feedstock and treatment) has increased.
Some of these findings are listed in table 1:

**Table 1. Findings of different studies on prospects and concerns of biochar amendment**

<table>
<thead>
<tr>
<th>Biochar feedstock</th>
<th>Treatment</th>
<th>Soil type</th>
<th>Prospects</th>
<th>Concerns</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mix of hardwood and hickory</td>
<td>Slow pyrolysis</td>
<td>Fine loamy</td>
<td>• Decrease of bulk density in bc treated fine loamy soil columns&lt;br&gt;• SSA in column increase from 130 to 153 m² g⁻¹ as biochar concentration increase.</td>
<td></td>
<td>(Laird et al., 2009)</td>
</tr>
<tr>
<td>Municipal green waste</td>
<td>Low temperature pyrolysis plant</td>
<td>Bauxite processing sand</td>
<td>• Increasing mesoporosity thus increasing available water and water content at field capacity</td>
<td>little or no effect on chemical properties</td>
<td>(Jones et al., 2010)</td>
</tr>
<tr>
<td>Wood residues</td>
<td>Earth mound method</td>
<td>Tropical soil</td>
<td>• Improved soil water permeability but also soil water holding capacity&lt;br&gt;• BC increased plant available P</td>
<td></td>
<td>(Asai et al., 2009);&lt;br&gt;(Glaser et al., 2002)</td>
</tr>
<tr>
<td>Hardwood trees(oak, cherry)</td>
<td>Intermediate pyrolysis (24 hours residence time)</td>
<td>Compacted sandy loam</td>
<td>• Increasing total C content (14.1 g kg⁻¹ in 0% biochar treatment and 21.7 g kg⁻¹ in 2% biochar treatment&lt;br&gt;• Biochar application increased water holding capacity&lt;br&gt;• Lower bulk density in 10% biochar application(0.84 g cm⁻¹) than 0% biochar application(0.95 g cm⁻¹)</td>
<td></td>
<td>(Case et al., 2012)</td>
</tr>
</tbody>
</table>

The findings in the table above are only a small fraction of the existing studies concerning the use of biochar in agricultural systems. As the interactions between soils and biochars are complex and still not fully investigated, this project focuses on the influence of different biochars on some important soil properties in different textured soils.
3 Project objectives

3.1 Main aim
To evaluate the influence of application of biochars, derived from different feedstocks and at different temperatures, on some chemical, physical and hydrological properties in different textured agricultural soils.

3.2 Hypothesis
1. Different biochars will imply different physical and chemical properties and based on that, behave differently in different textured soils.
2. The porous structure of biochar will enhance the soil water retention when mixed into the soil. The biggest effect on water retention capacity will presumably be seen in the sandy soil.
3. The irregular shape and the large particle sizes of the biochar, will alter the transport pathways, and possibly increase the nutrient retention.
4. The application of biochar will enhance the soil dissolved organic carbon and phosphorus pool.

3.3 Specific objectives
The specific objectives were to:
1. Characterize 11 biochars, derived from different feedstocks at different pyrolysis temperatures, for their potential to alter the soil chemistry in four different agricultural soils.
2. Quantify the effects of biochar application in different concentrations, on soil physical properties and soil water retention.
3. Investigate the capability of biochar in the soil, to reduce the leaching of colloids, DOC and phosphorus.

3.4 Structure of the thesis
This thesis is organized within different chapters. Each chapter starts with a small introduction, where the purpose of the chapter and background information is stated, followed by the materials and methods part.

The results are presented with either tables or figures. The discussion part is included in the result part. At the end of each chapter, a short sub-conclusion is formulated. In the very end a main conclusion is formulated and some perspectives and future considerations are presented.
4 Soils, biochars and biochar-soil mixtures

In the following chapters, different soils, biochars and biochar-soil mixtures are investigated for various soil functioning-properties. Therefore, the purpose of this chapter is to present and characterize these soils, biochars and biochar-soil mixtures. The physical and chemical composition of both soil and biochar gives a good first impression of some important functions, including soil water retention, saturated hydraulic conductivity, etc. (Brady, 2010).

4.1 Soils and soil texture

The experimental soils are three Danish agricultural soils from sites in Lundgaard, Askov, and Sdr. Stenderup (for location, see figure 6). The soils, are based on the Danish JB soil classification system, classified as JB1 (coarse sand), JB5 (Clayey sand) and JB7 (clay), respectively. For simplification reasons, the soils will be denoted as LUN (Lundgaard), ASK (Askov) and STEN (Sdr. Stenderup) in the report. The size and type of particles that make up the soil is referred to as soil texture. The texture of a soil determines the behavior of the soil, such as water holding capacity, nutrient retention, etc. and is therefore an important property (Brady, 2010).

The textural composition in percentage and the bulk density for the three soils is shown in table 2.

Table 2. Textural composition, bulk density, pH and EC for three Danish agricultural soils.

<table>
<thead>
<tr>
<th>Soil</th>
<th>JB</th>
<th>TOC</th>
<th>Organic Matter</th>
<th>Clay (&lt;2 µm)</th>
<th>Silt (2-20 µm)</th>
<th>Sand (20-2000 µm)</th>
<th>Bulk Density (g/cm³)</th>
<th>pH</th>
<th>EC (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lundgaard</td>
<td>1</td>
<td>0.76</td>
<td>1.3</td>
<td>3.1</td>
<td>1.7</td>
<td>94</td>
<td>1.6</td>
<td>5.9</td>
<td>584</td>
</tr>
<tr>
<td>Askov</td>
<td>5</td>
<td>2.3</td>
<td>4</td>
<td>8</td>
<td>6.8</td>
<td>81</td>
<td>1.34</td>
<td>5.3</td>
<td>587</td>
</tr>
<tr>
<td>Sdr. Stenderup</td>
<td>7</td>
<td>1.08</td>
<td>1.9</td>
<td>15</td>
<td>18</td>
<td>65</td>
<td>1.55</td>
<td>6.9</td>
<td>626</td>
</tr>
</tbody>
</table>

The LUN soil has the highest sand fraction accounting for 94 %, and hence a small clay and silt fraction. The sand fraction for the ASK soil is 81%, however it is notable that ASK soil has a high amount of organic matter (4%). Finally, the STEN soil has the largest clay and silt fraction.
4.2 Biochars and biochar characteristics

The 11 biochars used in this report were obtained from 6 different feedstocks, obtained by two different producers, namely the UK Biochar Research Centre and Frichs A/S (Denmark). Each feedstock material obtained by the UK Biochar Research Centre was derived from two different pyrolysis temperatures, 550 and 700°C respectively. The feedstock material (straw) from Frichs A/S was only pyrolysed at 750°C.

In table 3, all biochars are listed with feedstock material, pyrolysis temperature, pH, total carbon (TC) and total phosphorus (TP), declared by the producer. All biochars are alkaline, however, the biochars derived at 700 °C tend to have higher pH values. As for the pH, also the EC is higher in the biochars derived at 700°C, except for the wheat straw pellets. The values for TC and total TP are very diverse, ranging from 47.3-90.2 (total C wt %) and from 0.07- 0.29 (total P wt %), respectively. The variability for TC and TP can be attributed to the different feedstocks used, and the pyrolysis conditions.

Table 3. Biochar properties from producer (Geoscience, 2016) and own measurements (Nm=not measured)

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Proces Temp. °C</th>
<th>pH</th>
<th>EC (µS/cm)</th>
<th>Total C (wt%)</th>
<th>Total P (wt%)</th>
<th>Particle density (g/cm³)</th>
<th>Bulk density (g/cm³)</th>
<th>Air dried moisture content % (w/W)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft Wood Pellets</td>
<td>550</td>
<td>7.9</td>
<td>90</td>
<td>85.5</td>
<td>0.06</td>
<td>Nm</td>
<td>0.41</td>
<td>1.2</td>
</tr>
<tr>
<td>Soft Wood Pellets</td>
<td>700</td>
<td>8.4</td>
<td>160</td>
<td>90.2</td>
<td>0.07</td>
<td>1.52</td>
<td>0.39</td>
<td>1.79</td>
</tr>
<tr>
<td>Oil Seed Rape Straw Pellets</td>
<td>550</td>
<td>9.8</td>
<td>2270</td>
<td>68.8</td>
<td>0.29</td>
<td>Nm</td>
<td>0.31</td>
<td>2.09</td>
</tr>
<tr>
<td>Oil Seed Rape Straw Pellets</td>
<td>700</td>
<td>10.4</td>
<td>3110</td>
<td>67.7</td>
<td>0.26</td>
<td>1.82</td>
<td>0.36</td>
<td>3.29</td>
</tr>
<tr>
<td>Rice Husk</td>
<td>550</td>
<td>9.7</td>
<td>480</td>
<td>48.7</td>
<td>0.10</td>
<td>Nm</td>
<td>0.19</td>
<td>1.66</td>
</tr>
<tr>
<td>Rice Husk</td>
<td>700</td>
<td>9.8</td>
<td>690</td>
<td>47.3</td>
<td>0.16</td>
<td>Nm</td>
<td>0.20</td>
<td>1.26</td>
</tr>
<tr>
<td>Mischanthus Straw Pellets</td>
<td>550</td>
<td>9.8</td>
<td>820</td>
<td>75.4</td>
<td>0.19</td>
<td>Nm</td>
<td>0.35</td>
<td>1.6</td>
</tr>
<tr>
<td>Mischanthus Straw Pellets</td>
<td>700</td>
<td>9.7</td>
<td>1910</td>
<td>79.2</td>
<td>0.76</td>
<td>Nm</td>
<td>0.31</td>
<td>1.58</td>
</tr>
<tr>
<td>Wheat Straw Pellets</td>
<td>550</td>
<td>9.9</td>
<td>1700</td>
<td>68.3</td>
<td>0.14</td>
<td>Nm</td>
<td>0.36</td>
<td>1.7</td>
</tr>
<tr>
<td>Wheat Straw Pellets</td>
<td>700</td>
<td>10</td>
<td>1520</td>
<td>69</td>
<td>0.25</td>
<td>Nm</td>
<td>0.39</td>
<td>0.99</td>
</tr>
<tr>
<td>Straw</td>
<td>750</td>
<td>8.4</td>
<td>Nm</td>
<td>79.3</td>
<td>-</td>
<td>1.96</td>
<td>0.12</td>
<td>3.03</td>
</tr>
</tbody>
</table>

For simplification reasons the biochars will be referred to as, SWP 5 & SWP 7 for the soft wood pellets at 550 and 700°C, OSR 5 & OSR 7 for the oil seed rape straw pellets at 550 and 700°C, RH 5 & RH 7 for the rice husk at 550 and 700°C, MSP 5 & MSP 7 for the mischanthus straw pellets at 550 and 700°C, WSP 5 & WSP 7 for the wheat straw pellets at 550 and 700°C, and NIMA for the straw at 750°C.
Throughout the experiments, the biochar pellets were crushed and sieved down to 2 mm (figure 7) and determined for air dried water content by weighing small amounts (approx. 3x4g for each biochar) in trays and oven dried at 105°C for 24 hours.

Figure 7. Left; OSR biochar pellets before sieving, right; OSR biochar after sieving

The measured air-dried water content for all biochars in percent is listed in table 4. Here the OSR 7 and the NIMA biochar have the highest air-dried water content, accounting for 3.29 % and 3.03 % (w/W), respectively. For the RH, MSP and WSP the higher pyrolysis temperature had the highest air-dried water content (see table 3).

4.3 Specific surface area of soils and biochars

To find out, how much water the biochar is able to adsorb, the specific surface area (SSA) for all biochars and soils was measured. The SSA is an indirect measure of the capacity of a soil to retain water and nutrients (Carter et al., 1986), therefore the SSA determines many physical and chemical properties of the soil/or biochar particles.

4.3.1 Method

The SSA expressed per unit of mass (m²g⁻¹) was determined for all biochars and soils using the Ethylene Glycol Monoethyl Ether (EGME) adsorption method that measures the total surface area (internal and external). As described by Dyal and Hendricks (1950), the assumption is that 1 m² of clay surface with one molecular layer, is covered by 0.000286 g of EGME, therefore:

\[
SSA = \frac{W_a}{W_s \times 0.000286} \quad \text{Eq. [1]}
\]

\[
W_a = \text{mass of retained EGME in gram}
\]

\[
W_s = \text{mass of dried soil/biochar in gram}
\]

(Carter et al., 1986).
4.3.2 Results
The water retention, water movement, contaminant adsorption and ion exchange are closely related to the SSA of a particle. Generally, large sand particles have low SSA and hence little capacity to hold water or nutrients. Whereas small clay particles have large SSA, contributing most of the surface area to soils (Carter et al., 1986)

The SSAs that were measured for the pure biochars and the pure soils show big differences among each other (figure 8). Figure 8 shows, that for only the pure soils, the clayey STEN soil has the highest SSA (54.5 m² g⁻¹), which is due to its textural composition, containing 15 % clay and 18 % silt (table 2). The SSA of the ASK soil is 33.3 m² g⁻¹, and the sandy LUN soil has the lowest SSA, accounting for 11.5 m² g⁻¹. The SSA for the pure biochars are ranging from 214- 411 (m² g⁻¹), the trend is that the biochars derived at 550°C have larger SSA compared to the 700°C, with the exception of SWP where it is reverse.

Figure 8. Specific Surface Area (m² g⁻¹) determined by the EGME method for pure soils and pure biochars.

Many studies have shown that high SSAs of biochars can enhance the SSA of soils, when incorporated. Laird et al. (2010) found that the increasing concentration of hardwood biochar increased the SSA from 130 to 153 m² g⁻¹ in a fine loamy soil.

As mentioned before, the SSA is an indirect measurement of how much water soil/biochar can hold, therefore the SSA is plotted against the air dried water content (g H₂O/g DM) for the three pure soils and the pure biochars and is demonstrated in figure 9.

The air dried water content of the LUN, ASK and STEN soil accounts for 0.008, 0.02 and 0.015 g H₂O/ g DM, respectively. As expected, the sandy LUN soil has the lowest amount of air dried water content, due to its small SSA. However, one would assume that the STEN soil
with the largest SSA concurrently will have the highest amount of air-dried water content, but this is not the case, since the ASK soil has the highest amount of air-dried water content.

The suggestion, that the biochars will have a much higher water content due to the size of the SSA, could not be confirmed, since there is no clear correlation between the air-dried water content and the SSA for the pure biochars. The much larger SSA of the biochars (compared to the SSA of the soil) is in most cases no indication for a higher amount of air-dried water content. Only the OSR 7 and NIMA have higher air-dried water content compared to the pure soils (figure 9).

However, it is well known, that freshly made biochar are generally hydrophobic and contain few surface functional groups. It is first in the soil environment, where the biochar is exposed to water and oxygen, that the biochar surface oxidizes resulting in the forming of carboxyl- and other functional groups. This formation increases the cation exchange capacity turning the biochar into hydrophilic material (Laird et al., 2009). Recent studies recognized the hydrophobicity in fresh biochar produced at low temperatures (Laird et al., 2009). Kinney et al. (2012) observed decreasing hydrophobicity with increasing production temperature and found higher hydrophobicity at low charring temperatures (300°C) in 3 different feedstocks (corn stover, magnolia leaf and apple wood) compared to higher charring temperatures (400,500 and 600°C).

![Figure 9. The correlation between the air dried water content (g g⁻¹) and the SSA (m² g⁻¹) of pure soils and biochars.](image)

### 4.4 Particle density and porosity of soils and biochars

The particle density, or the density of solids, is defined as the ratio of the solid phase mass to the volume of the soil solid phase, expressed in g/cm³. The particle density for most mineral soils ranges from 2.60 to 2.75 g/cm³, and the particle density value 2.65 g/cm³ has been suggested as a characterization of a general mineral soil (Brady, 2010). Therefore, the particle density of the LUN, ASK, and STEN soil is assumed to be 2.65 g/cm³.
The particle densities of biochars (only SWP 7, OSR 7 & NIMA) were determined by the pycnometer method, and are listed in table 3. The particle density of the pure biochars (SWP 7: 1.52 g cm$^{-3}$, OSR 7: 1.82 g cm$^{-3}$ and NIMA: 1.96 g cm$^{-3}$) is notably lower, than the suggested 2.65 g cm$^{-3}$ for the pure soils. The density of biochar depends on the starting material and the pyrolysis process, and is very diverse (Lehmann and Joseph, 2009). Sun et al. (2015a) found a similar particle density (1.50 g cm$^{-3}$) for biochar derived from birch wood. They also found that biochar incorporated into soil (sandy loam), decreased the particle density, depending on the application rate.

The total porosity is an important property that results from the particle density and the bulk density, and represents the void space in a body of soil available for fluids and gases (Blume et al., 2009).

The total porosity ($\Phi$) was calculated from the differences in densities, bulk density ($\rho_b$) and particle density ($\rho_s$) by the equation:

$$\Phi = 1 - \frac{\rho_b}{\rho_s}$$

Eq. [2]

(Blume et al., 2009).

The total porosity of biochar varies, based on the production process and feedstock used. Hence, the creation of micropores is related to the creation of high surface areas (Rutherford and Wershaw, 2004). In general, the total porosity of biochar is high (Lehmann and Joseph, 2009). However, the development of pores in biochar is not well understood but may be related to the heating temperature and duration (Rutherford and Wershaw, 2004). Table 4 shows that the total porosity of pure soils is lower than the total porosity of pure biochars (only SWP7, OSR 7 and NIMA). The NIMA biochar has the highest total porosity accounting for 0.93.

Table 4. Total porosity of pure soils and biochars determined by equation 2.

<table>
<thead>
<tr>
<th></th>
<th>Total porosity ($\Phi$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LUN</td>
<td>0.40</td>
</tr>
<tr>
<td>ASK</td>
<td>0.49</td>
</tr>
<tr>
<td>STEN</td>
<td>0.42</td>
</tr>
<tr>
<td>SWP 7</td>
<td>0.74</td>
</tr>
<tr>
<td>OSR 7</td>
<td>0.80</td>
</tr>
<tr>
<td>NIMA</td>
<td>0.93</td>
</tr>
</tbody>
</table>
4.5 Characteristics of biochar and soil mixtures

To investigate how and if different biochars will influence some basic physical and hydraulic properties of the soils, we choose three different biochars from table 4, namely the SWP 7, OSR 7 and NIMA biochar. Each soil (LUN, ASK and STEN) was mixed with each biochar in four concentrations (0, 0.5, 1 and 2 %) and packed into 100 cm³ steel rings (the method is described in chapter 5.3.1). The bulk density (BD), which is the mass of solids per unit volume of a soil sample (g cm⁻³), is an important soil characteristic affecting the rainfall infiltration (Basso et al., 2013). Due to the low density of biochars, the application of biochar to each soil decreased the BD compared to the reference soil.

The NIMA biochar induced the most remarkable changes in BD in all soils, as for example the application of 2 % NIMA resulted in a decline of 16-17 % in all soils (figure 10 a). The trend in decreasing BD after biochar application has already been reported in many studies, as for example Laird et al. (2010), Lei and Zhang (2013), and Hardie et al. (2013) who measured a significantly lower BD in biochar amended soil columns. Peake et al. (2014) found that increasing biochar application rates (0.1, 0.5 and 2.5 %) decreased the BD in eight different soil types.

![Figure 10. Change in bulk density (A) and Total porosity (B) with 0.5,1 and 2% application of SWP 7, OSR 7 and NIMA to the LUN, ASK and STEN soils.](image)

The biochar-induced changes in the BD gave rise to increasing total porosity (figure 10 b). In general, the application of organic matter is suggested to improve soil aggregation, resulting
in increasing total porosity (Yakupoglu and Ozdemir, 2012). The increasing trend in total porosity after the application of biochar is confirmed by many studies, (Hardie et al. (2013); Basso et al. (2013)) and may also be due to the initial porosity of the biochars creating large pores in the surrounding soil (Hardie et al., 2013).

Sub-Conclusion
The biochars, derived from different feedstocks and produced at different temperatures, exhibit different characteristics.

- Large variability in nutrient composition among all biochars.
- All biochars have high SSAs ranging from 214 to 411 m² g⁻¹.
- The air-dried water content in biochar cannot be associated with the SSA of the biochars, presumably caused by hydrophobicity of the biochar surfaces.
- The increasing application of all biochars is decreasing the bulk density and increasing the porosity in all soils.
- In general, the 2% application of the NIMA biochar had the largest capacity to alter the bulk density and total porosity when incorporated into all soils.

5 Soil water retention
5.1 Introduction
The characterization of the soil hydraulic properties is important for many purposes, including agricultural and groundwater management (Schelle et al., 2013).

Soil water retention is a substantial hydraulic property that regulates soil functioning in ecosystems (Rawls et al., 2003), and it relates the matric potential of a soil to the water content, and thereby describing the pore-size distribution of a soil (Hillel, 1980).

The soil water, obtained by precipitation and to a minor degree from condensations, remains either as adhesive water in the soil (held against gravitational forces) or flows through it as percolating water, forming the groundwater.

The phenomenon called hydrogen bonding allows two water molecules to form a low-energy bond, and here two forces are responsible for water retention and movement in the soil: Cohesion where two water molecules attract each other, and adhesion (or adsorption) where water molecules attract to soil solid surfaces (e.g. clay minerals, organic matter). The forces of cohesion and adhesion cause capillarity (higher rise in small pores than in large pores), which allows water to move in any direction among fine pores. The capillary movement in the soil is determined by its pore size distribution (Brady, 2010).
Buckingham (1907) described the term “potential” in relation to the retention of water in soils. Whenever water is moving in the soil matrix, energy must be provided. This energy status of soils is termed as soil water potential, thus, water in the soil matrix moves from places with a high level of potential energy to places with relatively low potential energy levels. This concept of potentials can relate to the movements of infiltration, draining and capillary rise (Blume et al., 2009).

The soil water potential ($\psi$) can be ascribed as:

$$\psi = h \ (cm \ H_2O) \quad \text{Eq. [3]}$$

Where $h$ is the height of the pressure head.

(Blume et al., 2009).

In general, three important forces are suggested to affect the potential energy level of soil water and its availability for plants. The adhesion creating matric forces, the cohesion responsible for osmotic forces, reducing the energy state of water in the soil solution, and the gravity that always pulls the water downwards (Brady, 2010).

Furthermore, water in unsaturated soils appear in the pores, and in moisture films around soil particles (figure 11), and with increasing desiccation, the moisture is held tightly, in thin moisture films around the particles, which aggravates the movement of the water molecules.

![Figure 11. A moist soil with pores containing water and air. The larger pores have partly been drained, allowing the air to enter. Smaller pores are still filled with water.](image)

Due to differences in energy levels, different soil water potentials, including (gravitational ($\psi_g$), matric ($\psi_m$), hydrostatic ($\psi_h$) and osmotic ($\psi_o$)) potential, are relevant for understanding the behavior of water in soils. In unsaturated soils, the interaction between soil and water is omnipresent, therefore the matric potential is the most important factor determining the movement and availability of water through the soil matrix (Blume et al., 2009). It is noted
that in regions of high evaporation and low precipitation the osmotic potential may have a significantly influence on water-availability (Blume et al., 2009).

The relationship between the water content in the soil ($\theta$) and the soil water potential (tension) characterizes how much water a certain soil is able to retain at a given soil water potential (Mollinedo et al., 2015).

5.1.1 Soil water retention curve
The soil water retention curve (SWRC) is an important tool for modeling water flow and the transport of chemicals in soils and the behavior of soil water in unsaturated soils. It is especially crucial for agricultural management, hereunder irrigation practices (amount and timing of irrigation), and SWRC is strongly affected by soil chemical and physical characteristics, such as soil texture and structure, organic matter, and type of clay mineral, etc. (Jabro et al., 2008).

The water holding capacity of a soil is directly dependent on its pore size distribution. Hence, the smaller the pore diameter in a given soil, the higher the tension (in cm H$_2$O) with which the water is held.

The SWRC is the graphical line-up of the volumetric water content (volume basis) or the gravimetric water content (mass basis) against the matric potential ($\psi$). Since the potential suction of the soil water can be expected to reach values up to 100 000 cm H$_2$O, the suction (matric potential) is assigned as the logarithm of - cm water and is referred to as pF. Thus pF 1 corresponds to the tension 10 cm water. The water content at pF 0 corresponds to the void space in the soil, which is filled with water (saturation) after for example heavy rain or irrigation (Rowell et al., 2013).

Figure 12 illustrates how three different soil types will influence the behavior of the curve. In general, the higher clay content, the higher water retaining properties. The clayey soils will be able to hold on much more water at a given potential compared to loamy or sandy soils. This is because of the fine pores and the uniform pore size distribution in clay soils that can hold the water much more tenaciously than the relatively large pores in sandy soils. The flat shape of the retention curve for the sandy soil indicates that once the water has been
drained from the large pores, only a small amount of water will be present (Brady, 2010).

![Graph showing soil water retention curves for clay, silt loam & sand soil](image1)

**Figure 12.** Soil water retention curves for clay, silt loam & sand soil from (Tuller and Or, 2003). SWRC are used as an index of the available water in the soil, and can be helpful in classifying soils for irrigation purposes.

### 5.2 Method

#### 5.2.1 Preparation of 100 cm³ steel rings

For the determination of relevant soil hydraulic properties, we used the three different soils: LUN, ASK, and STEN, and the 11 biochars. The biochars were moistened with demineralized water in the ratio 2:1 (200 g biochar + 100 g dem. water) except for the RH 550 & 700 where 50 g biochar was moistened with 110 g H₂O.

Each soil was mixed with 0 %, 0.5 %, 1 % and 2 % of biochars SWP 700, OSR 700 and NIMA, and carefully packed into 100 cm³ steel cylinders, with a rubber ring and a nylon cloth on one end of the ring. Each treatment was run in triplicates (n=3). The pure biochars SWP 550 & 700, OSR 550 & 700, RH 550 & 700, MSP 550 &700, WSP 550 & 700 and NIMA were also packed into the 100 cm³ steel cylinders.

![Steps for preparing steel rings](image2)

**Figure 13.** From left to right; moistening, sieving, packing and saturation of steel rings with soil and biochar mixtures.
The packed soil samples in the steel rings were placed in sandboxes and slowly moistened with tap water for 4 days, and subsequently saturated with capillary water from underneath for a week. The process from moistening to packing and placing in the sandbox is illustrated in figure 13.

After one week, the soil columns were drained over a period of months to the matric water potentials -10, -30, -50, -100, -300, -500 and -1000 cm H$_2$O (corresponding to pF 1, 1.5, 1.7, 2, 2.5, 2.7 and 3) (the next matrix potential was aligned, when equilibrium occurred). For the matric potentials -300, -500 and -1000 cm H$_2$O, the soil samples were relocated into pressure chambers on ceramic plates, since the sandboxes are not able to create a tension above -100 (pF 2), due to the coarse texture of the sand (in the sandbox). At each potential, soil samples and steel rings were weighed, and at -30, -100 and -500 cm H$_2$O the air permeability and gas diffusion was measured on all samples, (due to time limitation, and aggravated handling of the soil samples due to very dry samples, measurements at matric potential -1000 were not possible). After determining the soil water characteristics (as illustrated in figure 14), the samples were again saturated for at least 3 days in the sandbox, and then measured for saturated hydraulic conductivity ($k_{sat}$). After all measurements, the samples were dried for at least 1 day and then weighed.

![Figure 14](image)

**Figure 14.** From left to right; weighing of soil columns at each matric potential, air permeability, gas diffusivity measurements and drying of soil.

### 5.2.2 Soil water content ($\theta$, w)

The gravimetric soil water content (g g$^{-1}$) was measured on all samples after completing relevant experiments. The samples were oven dried for minimum 1 day at 105°C, then immediately weighed. The gravimetric water content was then determined as the mass of water in each steel ring divided by the mass of oven-dried soil in the ring (w (g/g)) (Bruun et al., 2014).

Afterwards, the soil bulk density ($p_b$) was determined as the mass of oven dried soil in the sample divided by the total soil volume, which for the steel rings is 100 cm$^3$, ($p_b$; g cm$^{-3}$).
However, for the ASK and STEN soils and mixtures, the total soil volume was calculated to be 109 g cm$^3$, due to the assumption that the packed soil was swelling 3 mm over the steel rings. Volumetric water content (cm$^3$ cm$^{-3}$) was measured as described by (Bruun et al., 2014).

$$\theta = w \ast \rho_b / \rho_w$$  \hspace{1cm} Eq. [4]

Where $w$ is the gravimetric water content and, $\rho_b$ the bulk density and $\rho_w$ the water density (1.00 g cm$^3$)

The soil water content is expressed on a volume basis and mass basis in the result part.

The saturated volumetric water content (pF 0) is assumed to equal the calculated total porosity (described in chapter 4.4).

**5.2.2.2 Field Capacity and air filled porosity**

The field capacity is measured at pF 2.0, as noted by (Moldrup et al., 2000) and reflects the amount of water that will be held in the soil matrix by small and medium sized soil pores (equivalent diameters <30 µm) when free drainage by gravity is irrelevant. In other words, at field capacity the water has moved out of the large macropores and instead the air has moved in. The micropores are still filled with water that is available for plants.

Air filled porosity ($\varepsilon$) is the space in the soil allowing the flow of gases, indicating soil aeration conditions. It was calculated as the difference of total porosity and volumetric water content (Sun, 2015). It is assumed that the air filled porosity at pF 2.0 equals the volumetric content of large pores (>30 µm) (Moldrup et al., 2000).
5.3 Results

5.3.1 Soil water retention for pure soils
The SWRC for the three soils are illustrated in figure 15.

Figure 15. Soil water retention curves on a gravimetric (left) and volumetric basis (right) for the LUN, ASK and STEN soils.

Figure 15 depicts that the STEN soil is able to hold the water better than the two other soils, due to a higher clay content (Mollinedo et al., 2015). At field capacity (pF 2), the STEN soil is holding much more water than the other two soils, which is due to the small particles and hence finer pores in clayey soils.

The small surface area of the soil particles and the lack of fine pores can therefore explain the significantly lower water retaining capacity in the sandy LUN soil (Mollinedo et al., 2015).

5.3.2 Soil water retention for pure biochars
The SWRC for the pure biochars showed that the NIMA biochar had the highest water retention capacity compared to the 10 other biochars (figure 16) revealing that the different biochars have fairly varying water retaining properties, however (figure 16) shows the water retention capacity for the biochars that were used to mix with the soil. There can be observed a rapid decline in the volumetric water content for the SWP 7 biochar from pF 0 to 1.5, while both NIMA and OSR 7 are showing similar trends of water retention.
5.3.3 Distribution of air and water in pure soils and pure biochars at field capacity

Once the gravitational water is drained from the soil pores, the soil is said to be at field capacity (Whalen and Sampedro, 2010). Field capacity can be observed on the SWRC at pF 2 (Moldrag et al., 2000) and is defined as “the amount of water held in the soil after the excess gravitational water has drained away and after the rate of downward movement of water has materially decreased” (Veihmeyer and Hendrickson, 1931). Besides being important for establishing initial conditions for numerous hydrological models, field capacity is also considered for determining water-availability for plants (water content between field capacity and wilting point).

The distribution of air and water at field capacity, where the air filled porosity corresponds to the volumetric content of large pores (>30 µm), is illustrated in figure 17. For the pure soils, the volumetric water content is higher than the air filled porosity, however, the highest water content can be observed in the clayey STEN soil (0.39 cm³ cm⁻³) and the lowest in the sandy LUN soil (0.21 cm³ cm⁻³). Concurrently, the air filled porosity is highest in the sandy soil and lowest in the clayey soil, which can be attributed to the large pores in sandy soils that will drain rapidly, allowing the air to enter (Brady, 2010). In contrast, the pure biochars exhibit higher air filled porosities than water content at field capacity (figure 16). The most notable is the NIMA biochar, which has an almost equal distribution of air filled porosity and water content at field capacity.
5.3.4 Soil water retention for biochar amended soils

In general, the retention curves for the biochar-amended soils were closer together when the water content was illustrated in volumetric water content than in gravimetric water content. Results from the water retention curves for the biochar-amended soils show generally higher water contents (gravimetric and volumetric) with increasing biochar concentrations compared to the reference soils. Overall, a higher biochar input resulted in higher water retention, both on a volume and mass basis.
The application of all biochars to the sandy LUN soil increased the water content at all matric potentials, but especially the saturated water content, which is related to the soil porosity (Baiamonte et al., 2015) benefits from the application of biochar.

For example, the application of 0.5 %, 1 % and 2 % SWP biochar increased the saturated water content, with 1.7, 4.7 and 5.2 %, respectively. The 2 % application of OSR 7 and NIMA biochar resulted in increased volumetric water content at field capacity accounting for 10.9 and 11.5 %, respectively. The 2 % application of SWP 7 decreased the water content at field capacity with 11.2 %.

In figure 18 (c), the effect of both the pure biochar and the soil biochar mixtures on water retention is illustrated. Notable is the higher capacity of pure OSR 7 and NIMA biochar to...
retain water at all matric potentials, compared to the soil biochar mixtures. This can presumably be credited to the large surface area and porosity of biochar.

The sandy loam ASK soil showed increasing water content relative to increasing biochar application rates (figure 19 a).

If we look at the NIMA biochar, which had the strongest water holding capacity, the 0.5, 1, and 2 % of NIMA application increased the saturated water content compared to the reference soil, with 3.6, 6.8 and 15.1 %, respectively.

However, at field capacity the 2 % application of SWP 7, OSR 7 and NIMA biochar decreased the volumetric water content with 4.2, 2.1 and 9 %, respectively.
Figure 19 (c) clarifies, that the pure NIMA biochar still has a higher capacity to retain water, than the soil biochar mixtures. The pure OSR 7 and SWP 7 biochars still have a higher saturated water content compared to the soil biochar mixtures, but a lower capacity to retain water at higher pF compared to NIMA.

The SWRC for the clayey STEN soil is following the trend that increasing biochar application rates induces higher water contents at different matric potentials. The application of NIMA biochar triggers the most distinct increase in water content.

Figure 20. Soil water retention curves for the STEN soil with increasing biochar application, on a mass basis (a) for the pure soil and the increasing biochar concentrations, on a mass basis for the pure soil and the increasing biochar concentrations and the pure biochar (b) and on a volumetric basis for pure soil and biochar, and increasing concentrations of biochar.
At field capacity, only the OSR 7 biochar slightly increased the volumetric water content. The SWP 7 and NIMA decreased the water content at field capacity with 0.8 and 0.6 %, respectively.

The gravimetric water content (figure 20 a) however, showed higher water contents at field capacity with biochar. The 2 % NIMA biochar increased the water content at field capacity with 20.2 %.

In figure 20 c, it is observed that the pure NIMA biochar no longer has higher water retaining capacities compared to the soil biochar mixtures at all matric potentials. Especially at higher matric potentials (pF 2.5-3), the water holding capacity for the pure NIMA biochar is markedly lower compared to the soil biochar mixture. This is mainly due to the high clay content in the STEN soil, which contributes with fine pores.

**Biochar potential to modify the SWRC**

In general, the application of all biochars increased the water holding capacity in all soils, this indicates, that the application of biochar can alter the soil physical properties. The addition of biochar to soil can have direct and indirect effects on the water retention. The soil pore network will especially determine the dimension of water retention in the soil, and will be affected by, for example, the inherent porosity of biochar, creating micropores (<0.002) in the soil (Baiamonte et al., 2015).

Studies revealed that the high inner surface area is one explanation for increasing soil water retention. Lei and Zhang (2013) found an increasing trend in the soil water retention capacity as pyrolysis temperature increased and a higher water retention capacity in woodchip biochar compared to biochar derived from dairy manure. It is concluded, that a lower bulk density and higher surface area contributed to higher porosity and adsorption of water. Sun et al. (2015b) found an increasing water retention capacity in birch wood biochar treated sandy loam soil and attributed this phenomenon indirectly to the modified soil pore structure after biochar application. Sohi et al. (2009) pointed out that the increased water retention is one of the main reasons for increasing crop yields after biochar application.

**5.3.5 Distribution of air and water for biochar amended soils at field capacity**

At field capacity (pF 2), corresponding to the volumetric content of large pores (>30 µm), the increasing biochar application rate is slightly increasing the air filled porosity in all three soils (figure 21). This is in accordance to the increase in total porosity (chapter 4.4) that was observed with biochar application.
However, the most remarkable capacity for increasing the air filled porosity in all soils can be attributed to the NIMA biochar. For example, in the LUN soil, the NIMA both contributes with higher water content and air filled porosity at field capacity. The pure ASK soil had an air filled porosity of 0.16 cm$^3$ cm$^{-3}$, while the 2 % NIMA application to the ASK soil lead to an air filled porosity of 0.27 cm$^3$ cm$^{-3}$. Despite the fact that the air filled porosity is increasing in most soils after biochar application, the water content is relatively stable, especially in the STEN soil, this is a very important feature, since the amount of water, that a soil can hold against gravity is a very important parameter for plant growth (Mollinedo et al., 2015).

However, Prommer et al. (2014) found no significant effect on the air filled porosity with wood biochar treated soils compared to the unamended soil. Sun et al. (2015a) found no significant difference in air filled porosity in a 40 Mg ha$^{-1}$ biochar amended soil, but a slightly higher air filled porosity in a 100 Mg ha$^{-1}$ biochar amended soil compared to the reference soil. They

---

**Figure 21.** Air filled porosity (black) and Water content (grey) in cm$^3$ cm$^{-3}$ for the pure soils and the biochar-amended soil at field capacity (pF 2).
concluded this to be due to the biochar altering the geometry characteristics of the soil pore network.

5.3.6 Modeling soil water retention

Measurements of the SWRC is time consuming, and numerous models have consequently been developed to predict the SWRC based on more easy accessible soil-data, such as texture and bulk density. To simplify the parameter estimation, empirical models for the SWRC are based on as few parameters as possible. The aim is to find a soil water retention model that estimates the entire SWRC, based on narrow soil water retention measurements, and find a relationship that fits to different soil types (Loll and Moldrup, 2000). Campbell (1974) proposed a two-parameter SWRC model, the air-entry and a pore-network parameter $b$, as shown in Eq. (5):

$$\psi = \psi_e \left(\frac{\theta}{\theta_s}\right)^b$$

Eq. [5]

where $\psi$ is the matric potential, $\psi_e$ is the air-entry point, $\theta$ and $\theta_s$ is the volumetric water content and volumetric water content at saturation, respectively. The empirical parameter $b$ is found as the negative slope of the SWRC between pF 1 and pF 3 when log ($\psi$) is plotted against the log ($\theta$). The parameter $b$ represents the soil pore size distribution and water retention properties (Poulsen et al., 1999). Typical values for $b$ ranges from 1-5 for coarse sandy soils, 4-14 for loamy soils, and 10-20 for clayey soils (Loll and Moldrup, 2000).

Table 6 - Campbell $b$ values for bare soils (LUN, ASK, &STEN) and soils with 0.5 AND 2 % biochar application (NIMA & SWP)

<table>
<thead>
<tr>
<th>Soil Texture</th>
<th>$b$ [-]</th>
<th>Soil + biochar</th>
<th>$b$ [-]</th>
<th>Soil + biochar (2 %)</th>
<th>$b$ [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coarse sandy (LUN)</td>
<td>2.78</td>
<td>0.5 % NIMA</td>
<td>2.55</td>
<td>2 % NIMA</td>
<td>2.53</td>
</tr>
<tr>
<td>Sandy clayey (ASK)</td>
<td>3.37</td>
<td>0.5 % NIMA</td>
<td>3.42</td>
<td>2 % NIMA</td>
<td>3.06</td>
</tr>
<tr>
<td>Clayey (STEN)</td>
<td>5.68</td>
<td>0.5 % NIMA</td>
<td>5.33</td>
<td>2 % NIMA</td>
<td>4.37</td>
</tr>
</tbody>
</table>

The Campbell $b$ values for the pure soils and the biochar-amended soils are presented in table 6. The LUN soil has the lowest value of $b$ (2.78) and the STEN soil the highest (5.68). Compared to the reference soil, the increasing application rate of NIMA to all soils decreased the value of $b$. Sun et al. (2013) reported similar findings, where the application of 5 % birch wood biochar to a sandy loam soil decreased the Campbell $b$, however not significantly. They concluded that lower $b$ values may indicate that application of biochar promote a more well-structured soil with wider distribution of pore sizes where water drains more gradually per unit pF change (Sun, 2015). In figure 22 the SSA is plotted against the Campbell $b$ for
the pure soils and for the pure biochars. The pure soils are having a strong correlation ($r^2=0.9$) while the biochars are not very well correlated ($r^2=0.14$).

Figure 22. The SSA (m$^2$ g$^{-1}$) plotted against the Campbell $b$ parameter in the pure soils and pure biochars.

However, Petersen et al. (1996) found good correlation between the SSA and the Campbell parameter $b$ for 29 Danish agricultural soils, and high correlations ($r^2=0.86$) for 20 Danish subsoils. They underlined, that the high correlations in the 20 subsoils may be due to a more homogenous structure and similar macropores compared to the 29 topsoils.

The weak correlation for the pure biochars may be due to its excessive SSA however, it is also likely due to the pore-size distribution of biochar.

**Sub-conclusion**

The water retaining capacity of biochars obtained by different feedstock will not be the same.

- The application of different biochars to different textured soils will raise different SWRC with varying severities.
- The extend of the SWRC for the biochar amended soils, is larger on a gravimetric base compared to a volumetric base. Pierson and Mulla (1989) pointed out, that the gravimetric water content strongly relates with the size of the pores. Therefore, since the biochar amendment is increasing the gravimetric water content at all matric potentials, we assume that the biochar application may increase the space available for water in the soil.
- The 2 % NIMA application had the largest effect on the water retaining capacity in every soil.
- At field capacity, the increasing biochar application (all biochars) increased the air filled porosity in all soils.

6 Saturated hydraulic conductivity (\(K_{\text{sat}}\))

6.1 Introduction
When the soil pores, large and small, are completely filled with water, the saturated flow of water takes place. The saturated hydraulic conductivity (\(K_{\text{sat}}\)) is the amount of water per time that flows through a column of soil (Brady, 2010), therefore it is a very important soil hydraulic property, that has a major effect on many hydrological processes (e.g. infiltration, run off generation etc.) (Fu et al., 2015). The one–dimensional water flow in the \(K_{\text{sat}}\) can be described by Darcy’s law, and is a function of various parameters, including overall soil structure, soil texture, clay content, organic matter content and soil aggregation (Lim et al., 2016). The \(K_{\text{sat}}\) is dependent on soil structure, such as the size, shape, and distribution of the pores. In undisturbed soil, macropores, such as root channels or earthworm burrows, will significantly increase the \(K_{\text{sat}}\) of soils with low \(K_{\text{sat}}\), such as fine textured soils. In general, coarse soils tend to have a higher \(K_{\text{sat}}\) compared to fine-textured soils, leading to rapid water infiltration and drainage in coarse soils (Lim et al., 2016; Loll and Moldrup, 2000).

6.2 Method
The \(K_{\text{sat}}\) was determined on all samples using the “Constant Head Method”, as described by (Reynolds and Elrick, 2002). The samples were tightened for cracks between the soil and the steel ring (using a small knife) then placed in the apparatus (figure 23) and re-saturated with 0.1 M CaCl\(_2\). After approximately 2 hours, the samples were assigned to a constant hydraulic pressure difference. The water that flows through the samples for 15-30 minutes is captured in plastic flask and measured for weight.
The $K_{sat}$ can then be calculated using following equation,

$$K_s = \frac{VL}{(At(H_2 - H_1))} \quad \text{Eq. [6]}$$

Where: $V$: the volume of water in the plastic flask
$A$: the area of the ring
$(H_2 - H_1)$: the hydraulic pressure difference
$L$: the height of the sample
$t$: the time

(Koppelgaard, 2016).

6.3 Results

The $K_{sat}$ of the 3 soils used in the soil water retention experiment are illustrated in figure 24. The sandy LUN soil has significantly higher values (ranging from 17.4-29.6 cm/hour in the 3 replicates) than the finer textured ASK (ranging from 3.3-8.9 cm/hour in the 3 replicates) and STEN (ranging from 0.1-1.3 cm/hour in the 3 replicates). The results for the pure soils indicate that the $K_{sat}$ is highly influenced by the particle size of the soil.

High $K_{sat}$ indicate a rapid infiltration where dissolved nutrients easily can reach the groundwater without being attenuated (Lim et al., 2016). Heavy clay soils often need to be remediated to improve the infiltration to ensure crop productivity.
The $K_{\text{sat}}$ for the pure biochars (both 550 & 700°C) ranged from 56 cm/hour for the NIMA biochar to 505 cm/hour for the rice husk (550°C). The overall trend is here, that the biochars produced at 550°C show a higher $K_{\text{sat}}$ than the biochars produced at 700°C, except the MSP biochar where it is reverse (figure 25). However, (Lei and Zhang, 2013) found that soil treated with biochar produced at high temperatures (700°C) increased the $K_{\text{sat}}$. Interestingly, even if all biochars were sieved down to 2 mm, the $K_{\text{sat}}$ values were very diversely, indicating different structures depending on the feedstock used and the process temperatures.
In figure 26 the air filled porosity at field capacity (pF 2), corresponding to the volumetric content of large pores (>30 µm) is plotted against the log of K_{sat} for the pure soils and pure biochars. The good relation is indicating that the biochars with the biggest number of large pores (>30µm) also had the highest K_{sat}. For example, the RH (both temperatures) had the highest air filled porosity at pF 2 and the highest K_{sat} values.

![Figure 26. The air filled porosity (ε) at field capacity plotted against the log K_{sat} for the pure soils and pure biochars.](image)

Interestingly, the SWP 5 had a high K_{sat} in proportion to its relatively low air filled porosity at field capacity. Based on the increasing K_{sat} followed by the increasing air filled porosity at field capacity, it can be assumed that by the application of one type of biochar, one can govern how many extra-large pores and hence an increase in K_{sat} the biochar will bring to the soil. This can particularly become beneficial for heavy clay soils.

However, the impact of biochar applications on the K_{sat} in soils is a complex interaction between soil and biochar physical properties (Lim et al., 2016). Herath et al. (2013) found that the amendment of biochar (corn stover pyrolysed at 550°C) on a silt loam soil resulted in an increasing effect (139 %) on the K_{sat} compared to the control treatment. Others found a decreasing K_{sat} in biochar amended sandy soils (Brockhoff et al., 2010) or no effect (Laird et al., 2010). The K_{sat} values for the biochar-amended soils did not show a clear trend with increasing biochar concentration (figure 27). For the LUN soil, the biochar application overall seems to decrease the K_{sat} values but there seem to be no influence of increasing biochar application rate.
As for example will the 0.5 and 2 % application of OSR decrease the $K_{sat}$ value with 48 % and 56 % respectively, while the 1 % application decreased the $K_{sat}$ value with 35 %. The pure NIMA biochar had a rather low $K_{sat}$ value but still higher than for the pure LUN soil. Nevertheless, the application of NIMA biochar will decrease the $K_{sat}$ in the sandy LUN soil. Uzoma et al. (2011) discussed, that this decreasing effect in $K_{sat}$ after biochar application to a sandy soil may be due to the high specific surface area and numerous pores of the biochar that first have to be filled up with water before it drains down. The $K_{sat}$ values for the ASK and STEN biochar amended soils seem to increase compared to the reference soil. Lim et al. (2016) concluded that the $K_{sat}$ in biochar amended soils is significantly influenced by particle sizes of biochar and soil, and that the particle size distribution strongly controls the pore geometry. Figure 28 shows the air filled porosity at field capacity (pF 2) plotted against the log $K_{sat}$ for the soil-biochar mixtures.
Figure 28. The air filled porosity at field capacity ($\varepsilon_{100}$) plotted against the $K_{sat}$ for the soil biochar mixtures.

For the LUN and in a minor degree for the STEN soil, the large pores may govern the $K_{sat}$.

The ASK soil, with a high humus content (see table 2), had a very high water retention capacity (see figure 19), and seems to have a particularly tortuous pore structure already (see figure 28 showing high air filled porosity, but low $K_{sat}$). The application of biochar may to open up the pore system, and let the water flow through it more easily.

Sub-conclusion

In conclusion, the saturated hydraulic conductivity measurement is a fast and easy way, to determine the influence of particle size and rates of biochar application on the water movement through the soil profile (Lim et al., 2015).

- As expected, the sandy LUN soil had the highest $K_{sat}$ values, indicating a rapid water infiltration, and the clayey STEN soil had the lowest values of $K_{sat}$.
- The application of biochar decreased the $K_{sat}$ value in the LUN soil and mostly increased the $K_{sat}$ in the ASK and STEN soils.
- The increasing application of biochar did not influence the $K_{sat}$.
7 Gas phase parameters

The gaseous phase in soils is a complex system that is influenced by many factors, and is important for many soil functions, including greenhouse gas emission, plant growth and activities of microorganisms. (Sun, 2015; Schjønning et al., 2013) The spaces between the soil particles that are not occupied by water will be filled with gases that either are in contact with the atmosphere or marooned by solid particles and water. For that reason, whenever the water content in the soil decreases, soil air will increase and vice versa. Sufficient aeration is the prerequisite for a healthy root system and thus for effective plant growth, and it is suggested that when the air filled porosity falls below 20 % of the pore space, many processes (microbial activity, plant growth) will be inhibited (Brady, 2010). The transport and exchange of gases takes place by the convective or the diffusional flow. The processes involved in the convection and diffusion of gases are highly influenced by texture differences and the organic matter content of the soils (Arthur et al., 2012), but both convective and diffusional transport in the subsurface are governed by the gas transport parameter air filled porosity (ε) and the pore network characteristics (Masis, 2015). Gas diffusivity and air permeability at field capacity (pF 2.0) are characteristic properties that are affected by changes in the soil bulk density (Masis, 2015). The porous structure of biochar can, when incorporated to the soil, change the soil pore system and thereby influence the gas phase transport parameters.

7.1 Air Permeability

7.1.1 Introduction
The soil air permeability (k_a), is the ability of soil to conduct air by convective flow, (Arthur et al., 2012). It can occur as a result of pressure change, for example due to precipitation water that suppresses the air from small pores (Blume et al., 2009). The convective gas flow takes place in the larger, continuous pores (Moldrup et al., 2001), and is directly dependent on soil type and the air filled porosity (ε) (Moldrup et al., 2003). The air permeability is also directly related to the square of the diameter of the air filled pores in the soil, and is therefore suggested as a measure of pore continuity and pore organization (Lipiec and Hatano, 2003). The air permeability at a given matric potential is therefore a good indicator for the pore characteristics of soils (Iversen et al., 2001a).

7.1.2 Method
The k_a was measured on all samples at -30, -100 and -500 cm H_2O (pF 1.5, 2.0 and 2.7). It is a useful measurement for the characterization of soil pores and was measured by using an air permeameter, as described by Iversen et al. (2001b), where the soil sample was placed on a steal sieve, after pressing the soil from the edge of the steel ring to reduce the risk of preferential air flow. The air permeability-measuring chamber was then placed over the
sample, and the air sealing was inflated around the sample. The air flow through the sample, pressurized to -5 cm, was read on mechanical flow meters or, when the flow was too low to read, the electronic flow meter was used. The air permeability is, according to (Iversen et al., 2001b) comparable to the water flow in porous media, and can therefore be estimated via Darcy’s law, where flow is proportional to the permeability (Poulsen et al., 1999):

\[ q = \left( \frac{k}{\eta} \right) \left( \frac{\Delta p}{\Delta x} \right) \]

Eq. [7]

\( q \) = flux density

\( \eta \) = dynamic viscosity (N s m\(^{-2}\))

\( p \) = pressure, and \( x \) = distance in flow direction

Kirkham (1947) indicated, that the \( k_a \) in the laboratory can be calculated using an integration of Darcy’s law:

\[ Q = \frac{k_a \Delta p a_s}{\eta L_s} \]

Eq. [8]

Where \( Q \) is the volumetric flow rate (m\(^3\) s\(^{-1}\)), \( \Delta p \) is the pressure difference across the sample, \( a_s \) is the cross sectional area (m\(^2\)), and \( L_s \) will be the length of the sample (m). When integrating the flow and the pressure that was recorded, the \( k_a \) can be calculated as:

\[ k_a = \frac{\eta Q L_s}{A_s \rho_m g h} \times 10^{12} \]

Eq. [9]

Using the following constants:

\( \rho_m \) = the density of the manometer fluid; 998.2 (kg m\(^{-3}\))

\( g \) = acceleration of gravity ; 9.816 (m s\(^{-2}\))

(Corey, 1986)

7.1.3 Results

The \( k_a \) across the three matric potentials (pF 1.5, 2.0 and 2.7) for the pure soils (figure 29) showed that from pF 1.5 to 2 the convective gas flow is highest in the sandy LUN soil indicating the highest soil aeration. When the soils were drained to pF 2.7, the \( k_a \) in the clayey STEN soil increased tremendous from 2.1 µm to 56.9 µm, possibly indicating the creation of a highly connected pore network (Moldrup et al., 2003).
Figure 29. Air permeability in the pure soils at pF 1.5, 2 and 2.7. Error bars represent standard errors (n=3).

For the other two soils, there was only a slightly increase in $k_a$.

The trend for the $k_a$ for all pure biochars (figure 30) was similar at the three matric potentials.

There is no consistent trend in whether 550 or 700°C temperature biochar will have higher or lower $k_a$. Generally, the $k_a$ in the pure biochars is significantly higher than in the pure soils. However, for the three biochars used as soil application in the soil columns, the SWP 7 had the highest $k_a$ at all matric potentials, indicating a high number of large pores. The NIMA had the lowest $k_a$ among all biochars.

Figure 30. Air permeability in the pure biochars. (Left) all biochars, (right) Biochars SWP 7, OSR 7 and NIMA at pF 1.5, 2 and 2.7. Error bars represent Standard errors (n=3).

The application of different concentrations of SWP and OSR biochar, overall resulted in higher $k_a$ in all soils, with few exceptions (see figure 31) this was also found by Sun et al.
(2013) who, at field capacity (pF 2), observed significantly higher median values for $k_a$ in biochar amended sandy loam soil, compared to the reference. However, the NIMA biochar, with the lowest $k_a$ values in the pure condition (figure 30), also mainly decreased the $k_a$ when incorporated into the soil, for all soils.

Figure 31. Air permeability in the mixtures at pF 1.5, 2 and 2.7. Different colors indicate different concentrations of biochar application.

Since the $k_a$ is highly dependent on soil air-filled porosity ($\varepsilon$) (Moldrup et al., 2003), the plots of the two parameters for all soils with all three biochars in every concentration can be seen in appendix A. Overall, the higher air filled porosity, the higher $k_a$. This is in consilience with (Masís-Meléndez et al., 2014) who underlined that the convective flow preferentially will occur in water-drained pores.

The $k_a$ is affected by the application of biochar, and there are some extended ranges of values for the biochar amended soils compared to the reference soil. This is confirmed by the suggestion of (Moldrup et al., 2001) that the $k_a$ is sensitive to the whole air filled pore network structure.
Especially the decreasing effect of the NIMA biochar is clearly visible and as expected, taking into account that the NIMA had the highest water retention capacity, an almost equally distributed volumetric water and air content at field capacity (figure 17), and the lowest $k_a$ in the pure condition (figure 30).

The ratio of $k_a$ and the gas diffusivity (specified in chapter 7.2) can, according to (Møldrup et al., 2010) be described as $P = k_a / (D_p / D_o)$, where $P$ is a pore structure index (around 700 $\mu$m$^2$ in medium structured soils).

Based on the assumption of Buckingham (1904), that, $\varepsilon^2 = D_p/D_o$, leads to the relationship between the air filled porosity ($\varepsilon$) and the $k_a$:

$$k_a = P \varepsilon^2$$  \hspace{1cm} Eq. [10]

The relation between the air filled porosity and $k_a$ at field capacity (figure 32) for the pure soils and the pure biochars underlines a strong influence of the macroporosity on the $k_a$. This was also observed by Sun et al., (2013) who found that a 64 % increase in macroporosity in a biochar amended soil resulted in higher $k_a$ values.

![Figure 32. The relationship between the air filled porosity and $k_a$ at field capacity (pF 2) for the pure soils and the pure biochars. The regression line is based on equation 10 ( $P$ accounting for 700 $\mu$m$^2$).](image)

The pure SWP 5 with the lowest air filled porosity at field capacity of all biochars showed relatively high $k_a$ values (as already observed for the $K_{sat}$). This may indicate a continuous pore structure.
7.2 Gas diffusion coefficient

7.2.1 Introduction
The relative gas diffusivity coefficient \( (D_p/D_o) \), is the ratio of gas mixture in the soil, \( D_p \), and free air, \( D_o \), and describes the transport of gases by diffusion. Diffusional movements are controlled by a gradient in gas concentration, where molecules move from a region of high concentration to a region of low concentration (Sun, 2015). The soil gas diffusivity is dependent on soil structure, but in general, the gas diffusivity as a function of air filled porosity controls the gas transport in the soil, as for example soil aeration or diffusion of greenhouse gases (Moldrup et al., 2000). Gas diffusivity is an important parameter for gas transport in soils representing the tortuosity and connectivity of the pores (Masís-Meléndez et al., 2014).

7.2.2 Method
Gas diffusion was measured on all samples at -30, -100 and -500 cm H\(_2\)O after air permeability measurements. The gas diffusion was measured by a non-steady state method as described by Schjønning et al. (2013) and Ball et al. (1981).

The apparatus consists of 12 parallel measuring chambers as shown in figure 3.3.

![One-chamber method set up. An oxygen sensor is located in the top (from Schjønning et al., 2013).](image)

Before the measurement, all chambers were calibrated at atmospheric air concentration by fanning until the oxygen sensors (figure 3.3) showed a stable value (approx. 20%). Then the nylon cloth and rubber was removed from the sample and replaced with a large rubber ring. The sample was placed on a steel mesh and was, together with a lid screwed tight to the chamber, to avoid any leakage. When all 12 samples were placed correctly, the inlet and
outlet valves were opened on each chamber and the chambers were flushed with nitrogen gas (N\textsubscript{2}) at a pressure of 1 bar, for calibration at 0 % air. When stability was attained (2-3 minutes) the valves were closed, first inlet then outlet for each chamber, respectively. The oxygen concentration in each chamber was measured automatically, and stopped when oxygen concentrations were at about 10-15 %, and then transferred from the “Lab-View-system” to an excel file. Fick’s law can describe the diffusivity through the soil sample, and the O\textsubscript{2} diffusion coefficient can be explained as the relation between time (approx. 120 min.) and the logarithm of the change in O\textsubscript{2} concentration at any given time. In the laboratory, the \( D \) was calculated from the equation:

\[
D_p = -h_s h_c K \quad \text{Eq. [11]}
\]

Where \( D_p \) is the diffusion coefficient of the soil (L\textsuperscript{2}T\textsuperscript{-1}), \( h_s \) the length of the soil sample or the diffusion pathway (L), \( h_c \) is the height of the diffusion chamber (L) and K the slope of the relation between the diffusion time and the logarithm of the change in concentration between the chamber and the atmosphere. The oxygen diffusion (\( D_o \)) in free air is 0.205 cm\textsuperscript{2} air s\textsuperscript{-1} (Schjønning et al., 2013).

**7.2.2.1 Relative gas diffusivity**

Relative gas diffusivity was expressed as \( D_p/D_o \), and was plotted against the air filled porosity, to identify and clarify the relationship between the two parameters.

In 1904, Buckingham did an approach for the prediction of gas diffusivity based on the air filled porosity (Moldrup et al., 2004). They suggested that the diffusion coefficient in soils is proportional to \( \varepsilon^2 \) (Buckingham, 1904).

\[
D_p/D_o = \varepsilon^2 \quad \text{Eq. [12]}
\]

However, it is basically impossible to estimate the diffusivity in all soils based on a single model, and ever since the Buckingham (1904) model is not a good fit for our data, we used:

\[
D_p/D_o = \varepsilon^{2.5} \quad \text{Eq. [13]}
\]

**7.2.2.2 Gas derived pore tortuosity**

The gas derived pore tortuosity (\( X \)) was calculated from the measured air filled porosity (\( \varepsilon \)) and the relative gas diffusivity, \( D_p/D_o \), at matric potential pF 2, using the equation based on the Buckingham (1904) model:

\[
X = \frac{\log\left(D_p/D_o\right)}{\log(\varepsilon)} \quad \text{Eq. [14]}
\]
The parameter X is used to describe the pore network connectivity (Deepagoda et al., 2012), and high values of X indicate a more tortuous pore system (Sun et al., 2015b).

### 7.2.3 Results

The relative gas diffusivity at field capacity and above (pF 2.7) was highest in the sandy LUN soil with 0.026 and 0.110 $D_p/D_o$, respectively. The lowest $D_p/D_o$ was measured in the clayey STEN soil, accounting for 0.003 and 0.025 at pF 2 and 2.7, respectively.

Overall, the $D_p/D_o$ was higher with biochar application. At field capacity, the increasing application rate of SWP and NIMA biochar increased the $D_p/D_o$, as for example the 2 % NIMA application increase the $D_p/D_o$ in the LUN soil with 57 %, compared to the reference. In the clayey STEN soil, the OSR and NIMA application increased the $D_p/D_o$ strongest at pF 2.7. Nevertheless, 2 % NIMA application to the STEN soil increased the $D_p/D_o$ at pF 2 and pF 2.7 with 75.5 and 78.8 %, respectively. The 0.5 and 1 % NIMA application did not increase the $D_p/D_o$ in the STEN soil. However, biochar application was most beneficial in the sandy loam ASK soil, where the increasing application rate of all biochars increased the $D_p/D_o$ at matric potential pF 2 and pF 2.7. Sun et al. (2013) also found extended ranges for the relative gas diffusivity in a sandy loam soil after biochar application, with the highest relative increase at field capacity.

The gas derived pore tortuosity (X) at field capacity (pF 2) is showing inconsistent pattern for the increasing application rate of biochar OSR and SWP, where it seems that the 0.5 % application is decreasing the X in all soils (except the SWP in the LUN and the NIMA in the STEN soil), while the 1 and 2 % application is slightly increasing or the same compared to the reference soil, in all soils (figure 34).

![Figure 34](image.png)

**Figure 34.** The gas derived pore tortuosity factor X for the mixtures. Different colours are indicating the application concentration of biochar. Error bars represent the standard error ($n=3$).
The NIMA biochar tends to increase the pore tortuosity in every soil, but only in the ASK soil, the trend is increasing with increasing NIMA application rate. Moreover, the gas derived pore tortuosity in the pure biochars is highest in the NIMA biochar. Based on the high water retention of the NIMA biochar and the equally distributed air filled porosity and water content at field capacity (figure 17) it can be assumed that the increasing tortuosity in soils, amended with the NIMA biochar, is caused by the high water content which is creating water bridges and in that way make it more complicated for the gases to flow through the pore system (Sun, 2015).

Figure 35 demonstrates the positive correlation between gas diffusivity and air filled porosity at pF 1.5, 2 and 2.7 for the pure soils and pure biochars, where the values are generally following a power function.

The dashed line showing the Buckingham (1904) model fit that originally was developed for the prediction of soil gas diffusivity in variably textured, natural intact soils is overestimating our values. This may be because it only is a function of the air filled porosity, without considering soil type or other parameters. Especially the values for the pure biochars are highly overestimated with the Buckingham (1904) model, which may be related to the porous and complex structure of biochar.

![Figure 35. The relationship between the air filled porosity and the relative gas diffusivity at field capacity. The dashed line is based on the assumption of Buckingham (1904), that $D_p/D_0 = \varepsilon^2$, the solid line is an alteration of the Buckingham (1904) assumption.](image-url)
In general, the relationship between the $D_p / D_o$ and air filled porosity in the mixtures, was not influenced by the biochar application rate (figure 36). Rather, the biochar extended the rate of air filled porosity and $D_p / D_o$, as already found in a study by Sun et al. (2013).

As already noted by Buckingham (1904), plots of $D_p / D_o$ and air filled porosity are no indication for the effect of the soil type. Moreover the $D_p / D_o$ is generally not dependent on the pore sizes in the soil (Chamindu Deepagoda, 2012). Therefore, the effect from the application of biochar may not be as significant for the $D_p / D_o$. 

Figure 36. The relationship between the air filled porosity and the relative gas diffusivity at pH 1.5, 2 and 2.7 in the biochar soil mixtures, different colors indicate different concentrations of biochar application. The dashed line is based on the assumption of Buckingham (1904), that $D_p / D_o = \epsilon^2$, the solid line is an alteration of the Buckingham (1904) assumption.
Sub-conclusion

The gas phase transport in a soil matrix is an important factor, influencing the soil aeration, and highly dependent on soil pore characteristics, including the total porosity, pore size-distribution, the shape of the pores, and tortuosity. To see if the application of biochar will alter the gas phase transport in soils, it is therefore highly important to elaborate both the convective and the diffusional gas transport, especially at a given air filled porosity.

8 Potential release of dissolved organic carbon (DOC) and phosphorus (P)

8.1 Introduction

The application of biochar will not only alter the physical properties of the soil (as described earlier) but has also been proposed to alter a range of soil chemical properties (Glaser et al., 2002). In this chapter, 11 biochars are examined based on the proposed capacity of biochar to alter important chemical properties when incorporated in the soil, and investigated for the maximum release of dissolved organic carbon (DOC) and phosphorus (P) under controlled conditions. The potential for biochar to modify the soil environment and release or retain nutrients has been linked to its large surface area, and an increase in porosity, water retention, cation exchange capacity and pH (Guo et al. (2002); Abel et al. (2013)).

8.2 Methods

To characterize chemical properties and to estimate the potential release of nutrients from the pure biochars and the soil-biochar mixtures, we conducted a batch experiment, where we used the 3 previous soils (LUN, ASK, STEN) plus a new one from Jyndevad (JYN) and the eleven biochars, which are described above. For the soil-biochar mixtures, 2% biochar was mixed with soil. The soil JYN is classified as coarse-grained sand with relatively high organic matter content, accounting for 3.1% (table 5).

Table 5. Soil properties for the JYN soil from (Masis, 2015).

<table>
<thead>
<tr>
<th>Soil</th>
<th>Organic Matter (%)</th>
<th>Clay (&lt;2 µm, %)</th>
<th>Silt (2-20 µm, %)</th>
<th>Sand (20-2000 µm, %)</th>
<th>Bulk Density (g/cm³)</th>
<th>pH</th>
<th>EC (µS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jyndevad</td>
<td>3.1</td>
<td>4</td>
<td>5</td>
<td>91</td>
<td>1.42</td>
<td>6</td>
<td>612</td>
</tr>
</tbody>
</table>
Five gram of either pure soil, pure biochar or a mixture of soil and biochar was weighed into plastic centrifuge tubes. We added 5 ml artificial soil water (0.652 mmol L$^{-1}$ NaCl, 0.025 mmol L$^{-1}$ KCl, 1.842 mmol L$^{-1}$ CaCl$_2$, 0.255 mmol L$^{-1}$ MgCl$_2$) into the samples, then placed the samples in a dark 2°C room, to ensure that the soil was wetted homogeneously. After 1 week, we added another 25 mL of soil water to the samples corresponding to a soil: water ratio of 1:6 (weight/weight), and placed them in a shaker at 30 rpm for 24 hours. After removing the samples from the shaker, the pH was measured using a pH meter with a glass electrode and the EC was measured in units of milliSiemens per centimeter (mS/cm) on a conductivity meter, then the samples were centrifuged at 5000 rpm for 60 minutes. The supernatant of each sample was carefully filtered through a 45 µm filter, and analyzed for DOC and P.

8.2.1. DOC measurement
DOC was measured on a total organic carbon analyzer (Shimadzu TOC-VCPH) using the NPOC method (non-purgeable organic carbon), where the samples are acidified down to pH 2-3 with hydrochloric acid and sparged with sparge gas to eliminate inorganic carbon, and then measured for total Carbon (Shimadzu, 2016).

8.2.2. P measurements
Total phosphorus was determined on 5 mL of the filtered supernatant, acidified with 50 µL 4M sulphuric acid and 1 mL persulfate for digestion in an autoclave (120°C, 200 kPa, 30 min.) (Koroleff, 2011) After autoclaving, we added 200µL ascorbic acid and PI reagent for colorimetric technique (Murphy and Riley, 1962). The P concentrations were calculated from standard curves based on standard row concentrations, prepared from 2 mL of 50 ppm (mg L$^{-1}$) (see figure 38).
8.2.3. Statistical analysis
Statistical analysis was conducted with the software SigmaPlot, where the interaction between the pure soil and the soil biochar mixtures were analyzed with the two-way anova test. Linear relationships between pH and DOC and pH and P were evaluated using the Pearson’s correlation coefficient $r$.

8.3. Results

8.3.1. Biochar effect on pH
The amount of hydrogen ions in a soil solution is reflected in the pH. So whether a soil is acidic, neutral or alkaline is determined by the concentration of free hydrogen ions in the soil solution. If the concentration of free hydrogen ions is high, the ground is referred to as acidic. The pH is particularly important in soils because it is an easy measurable parameter and has an influence on other soil properties and the soil microbial community. The pH values for the soils used in this study, ranged from pH 5.3- 6.9 (Figure 39a).

The pH values for the different soils, obtained by the batch experiment were significantly different, and the clayey STEN soil had the highest pH value.

![Figure 39. pH values for different soil types (a) and different biochars (b). Error bars are representing the Standard error (n=3) Means followed by the same letter are not significantly different at $p<0.05$.](image-url)
The pH values for the 11 different biochars were all alkaline ranging from 8.8 for the SWP 5 to 9-10 for the remaining biochars (Figure 39b). The biochars produced at higher temperatures, had higher pH values, this is in agreement with other studies (Yuan et al., 2011, Wu et al., 2012). The increased alkalinity of biochars may be caused by the loss of organic functional groups (such as –COOH and –OH) on the biochar surface at high temperatures (Zhang et al., 2015). Yuan et al. (2011) found an ignition loss of –COO at 700°C.

Moreover, the pH of biochar is dependent on the type of feedstock. For example, Yuan et al. (2011) found different pH values for straw biochar derived from different feedstocks, hereunder corn, peanut, canola, and soybean accounting for pH 9.4, 8.6, 6.5 and 7.7 respectively, under the same pyrolysis temperature (300°C).

The alkalinity of biochars and its liming effect in acidic soil has been proved in several studies (Chintala et al., 2014, Zhang et al., 2015), but depending on the feedstock used and the pyrolysis temperature, each biochar will have different liming potential.

The pH in the soil-biochar mixtures still followed the same trend as in the pure soils, see figure 40. The lowest pH values were observed in the ASK mixtures (ranging from pH 5.3 to 6.1) and the highest in the STEN mixtures (ranging from pH 6.9 to 7.1).

Figure 40. pH values for the soil biochar mixtures. Error bars are representing the Standard error (n=3) Asterisks indicate statistically difference between biochar amended and reference soil at p<0.05.

The more distinct change in pH in the coarse-textured soils (LUN and JYN) compared to the fine textured soils may be due to a lower buffering capacity against changes in pH in the coarse textured soils (Soinne et al., 2014).
However, most of the biochar soil mixtures show a significant difference in pH compared to the pure soil. The most remarkable increase in pH in all soils is observed with the OSR (550 & 700 °C) and the WSP (550 & 700°C) mixtures. The accumulation of cations (K, Na, Ca and Mg) and the formation of carbonates, such as CaCO₃ and MgCO₃ during pyrolysis of biochar, are responsible for the liming capacity of biochar. The organic anions of the biochar will rapidly react with H⁺ in the soil, while the carbonates will react slower with the H⁺, therefore the reduction of soil acidity will last longer (Yuan et al., 2011).

### 8.3.2 Biochar effect on electrical conductivity

The electrical conductivity (EC) can be used as an index for ionic strength (Kumari et al., 2014), and is an estimate for the amount of dissolved salts in the solution (Hossain et al., 2011). Figure 41a shows that the EC measured in the batch experiment was similar for the 4 soils, ranging from (ranging from 583 to 625 µS/cm.).

For the pure biochars, there is a consistent tendency that the biochars produced at higher temperatures had higher EC (figure 41b). In general, the EC for the pure biochars were higher compared to the pure soils, which might mainly be due to presence of higher soluble salts in pure biochars (Chintala et al., 2014), caused by the loss of volatile materials (Gai et al., 2014). For the OSR, MSP and WSP biochars, the difference between the temperatures was significant.
In the mixtures (figure 42), The SWP (550 and 700°C) increased the EC in all soils (but only significantly in the sandy LUN soil), presumably due to its high EC in pure condition (figure 41b).

![Figure 42. EC values for the soil biochar mixtures. Error bars are representing the Standard error (n=3) Asterisks indicate statistically difference between biochar amended and reference soil at p<0.05.](image)

8.3.3 Biochar effect on DOC release

The dissolved organic carbon (DOC) is the fraction of the total organic carbon that can pass through a filter of 0.45 µm. It originates from the soil organic matter fraction, and is highly mobile (Bolan et al., 2011). The understanding of the dynamics of DOC in the soil environment is crucial, since it takes part in in many biogeochemical processes, such as carbon cycling and the facilitated transport of pollutants (Buckingham et al., 2008). The mobility of DOC is governed by the sorption to clay surfaces and Fe/Al oxides, which is dependent on the soil pH, average molecular weight of the DOC, C content of the soil and surface soil characteristics (Bolan et al., 2011).

The DOC release for the pure soils ranged from 0.84 to 2.1 mg DOC/ g soil (figure 43a). The highest amounts of DOC are present in the ASK and in the JYN soil, this is in corroboration with the high amounts of humus (see table 2) in the soil.
Shen (1999) described, that the initial organic matter content (as seen in the ASK soil) may hinder the sorption of further DOC due to blocking of active sites on the soil surface, and that the capacity to adsorb DOC is positively related to the clay content in the soil.

The amount of DOC in the pure biochars (figure 43b) was consistently higher at low temperatures (550°C) than at high temperatures (700°C). This is also described by Kumari (2015) and Liu et al. (2015) who found that biochars produced at high temperatures, resulted in lower DOC concentrations. The OSR (both temperatures) showed the highest DOC release values in the batch experiment, this can further be supported by the high native total C content (85.5 & 90.2 wt %) (Table 3).

When biochar is incorporated into the soil, the native DOC content in the pure biochar will directly increase the soil organic matter pool. Smebye et al. (2016) found higher DOC values in biochar soil mixtures (containing 10 % biochar) compared to the sum of the soil and biochar control. Therefore, they suggest that biochar induces a release of the soil native DOC and related this with the increase in pH.

The increasing pH may cause deprotonation of functional groups on the DOC molecules and thus increase the charge density and its hydrophilicity, resulting in more soluble DOC. Moreover, the release of DOC is governed by changes in the soil matrix, since the sorption of the negatively charged DOC mainly occurs on positively charged sites on the soil surfaces. Hence, an increasing pH will increase the negatively surface charge by deprotonation of the positive and neutral charged functional groups on the soil surface, and result in desorption of DOC (Smebye et al., 2016). Shen et al. (1999) found that the sorption of DOC will peak at pH 4-5 and decrease with further increasing pH.
The DOC values in the mixtures of the batch experiment (figure 44) were not as high as the sum of the reference biochar and reference soil, as stated by Smebye et al. (2016), that may be due to the much lesser biochar dosage (2 %) we used, compared to the 10 % biochar application in Smebye et al. (2016).

However, there are some biochars, including the SWP (both temperatures) that enhanced the release of DOC in the soil. Some of the other biochars apparently decreased the DOC release in some soils such as the SWP (both temperatures). This is in agreement with Mukherjee et al. (2011), who found a decrease in DOC in similar batch experiment with biochar applications, suggesting the capacity of biochar to sorb DOC.

### 8.3.4 Biochar effect on Phosphorus release

The role of phosphorus (P) is crucial in soils to maintain plant growth. For many years, excessive application of P fertilizers beyond plant requirements, has led to increasing P concentrations in the soil and eventually, due to runoff, erosion and leaching, in surface and groundwater, resulting in accelerated eutrophication. Therefore, it is necessary to evaluate new strategies that can provide P in forms that are available for plants but present a low risk for the environment. The P in the soil exists in inorganic and organic forms, where the inorganic P forms are extremely reactive and are present in many different mineral forms, representing the plant available P. The P mineral solubility is influenced by factors including, soil pH, concentration of Al, Fe, Ca and Mg, and the surface area of soil particles, as P is adsorbed to clay surfaces (Chintala et al., 2013).
As illustrated in figure 45, the fixation of P in soils occurs in different intervals. The hills in figure 45 are indicating the highest P fixation, thus the highest fixation of P will occur in acidic soils with pH less than 5, where the P will be adsorbed to iron and aluminum minerals.

Figure 45. Hills and valleys of phosphorus fixation in soils, from (AgSource, 2015)

The highest phosphorus availability will occur when the soil pH is between 6 and 7 (figure 45).

The P release from a soil, is controlled by its rate of dissolution, desorption and diffusion. A highly sorptive soil will release P slowly in the soil solution and vice versa, but the concentration of P in the soil solution is mainly affected by the quantity of P in the soil (McDowell et al., 2001).

The P concentration in the solution of the four examined soils ranged from 0.0011 to 0.0033 mg P per g soil, where the sandy LUN soil had the lowest concentration and the ASK the highest (Figure 46a). All soils show significant different P concentrations among each other.
Figure 46. P concentrations in different soil types (a) and different biochars (b). Error bars are representing the standard error (n=3) Means followed by the same letter are not significantly different at p<0.05.

The release of P from the pure biochars showed large variations, with concentrations ranging from 0.0037 mg P/g soil for the SWP 7 to 0.08 mg P/g soil for the NIMA. However, the high value for the NIMA biochar is exceptional high compared to the other biochars (see figure 46b). The concentration of P in the biochar is highly dependent on the nature of the feedstock used as well as the process temperature (Lehmann and Joseph, 2009).

There is no obvious trend that might indicate higher or lower P concentrations in high or low pyrolysis temperature biochars. However, the P concentration in the solution of the pure biochars originates from the native P pool in the feedstock used. Qian et al. (2013) found that the release of P from rice husk derived biochar to soil solution was influenced by several factors, as retention time, coexistence anions and other nutrient elements. The coexistence anions, as for example Cl⁻, NO₃⁻ and SO₄²⁻, that were introduced into the solution, significantly influenced the release of P from the biochar, due to competition of active sites on the biochar between the P and the added anions. Morales et al. (2013) explained, that higher pyrolysis temperatures will cause losses of volatile compounds in the biochar structure, and thus while the biochar yield decreases, the biochar surface increases and its functional groups that are responsible for the exchange capacity will decrease. This change in the quantity of functional groups on the SSA will influence the P sorption and desorption (Morales et al., 2013).

Recently, studies have shown, that biochar application to soil can influence the P availability, and hence can function as a reservoir for P with fractions of P available for plants (Zhang et al., 2015). Many studies on biochar as a soil amendment are based on its capacity to retain P or increase the amount of plant available P in soil after fertilizer application (Qian et al., 2013).
Laird et al. (2010) found a decreasing P release with increasing biochar concentration in manure amended soil columns. However, depending on the feedstock and the pyrolysis process, biochar may in itself be a potential P source, when incorporated into the soil, and likewise the ability to retain P will vary among the different biochars (Zhang et al., 2015).

The biochars mixed with soil (figure 47), generally increased the P release to the solution, except from in the ASK soil, where most biochars generally decreased the release of P. Interestingly, the SWP (both temperatures) biochar is decreasing the P concentration in the solution in all soils. An explanation for this decreasing trend, could besides its low native P concentration (figure 46b) also be a high sorption capacity.

![Figure 47. P concentrations in the soil biochar mixtures. Error bars are representing the standard error (n=3) Asterisks indicate statistically difference between biochar amended and reference soil at p<0.05.](image-url)
The influence of pH on DOC and P release

As already stated, biochar is increasing the soil pH when incorporated to the soil, and may therefore modify the mobility of nutrients in the soil. Based on the assumption of Smebye et al. (2016), that the release of DOC indirectly is influenced by the increasing pH after biochar application, the correlation between pH and DOC concentration in the solutions is illustrated in figure 48a. We found only a strong correlation between the pH and the DOC in the sandy LUN ($r^2=0.76$) and JYN ($r^2=0.78$) soils.

For the LUN soil, the biochar-induced increase in pH from 5.9 (pure soil) to 7.2, enhanced the DOC release mainly due to the dissolution of organic matter.

Due to the low clay content (3.1 %) the soil is not able to adsorb the released amount of DOC. The same trend is observed in the JYN soil, but with higher DOC values, due to the higher initial organic matter content in the JYN compared to the LUN (3.1 and 1.2 %, respectively).

The ASK soil has the largest amount of organic matter (4 %) and the release of DOC is therefore comparable with the JYN soil, however the range of pH is much lower (5.3 to 6.2),

Figure 48. The relationship between the pH and DOC release (a) and the pH and P release (b) in the pure soils (stars), and the soils mixed with different biochars (different colors).
so the dissolution of organic carbon is lower, and the relatively high clay content (8 %), might fixate the DOC molecules. The increase in pH in the STEN soil is relatively low, indicating a high buffer capacity. The large clay content (15 %) can easily fixate the organic matter (1.9 %) in the STEN soil. Presumably, more DOC will be released if extreme increases in pH occurs.

According to figure 48b, only the P release in the LUN and the STEN soils is influenced by the increasing pH. The LUN soil had a low initial P content (figure 46b), therefore the application of biochar (with a relatively high initial P content) will cause an increase in soil pH and thus the availability of P in the soil solution. The ASK soil had the highest initial P content. Interestingly, since the application of biochar only increased the pH from 5.3 to 6.2, the P is not available, according to the P fixation diagram as showed in figure 45, but will more likely be retained. The STEN soil has a high amount of clay (15 %) that can easily fixate P on the mineral surface, the initial P content in the biochar and the biochar-induced change in the pH may increase the P release. The P release in the JYN soil is not affected by the pH, indicating a sorption capacity for P at this pH range. The sandy JYN soil had unlike the sandy LUN soil a high amount of organic matter (3.1 %). This indicates that most of the released P was associated with the initial soil organic matter.

Conclusion

- The pH and EC is higher in biochars produced at high temperatures (700°C) compared to the biochars produced at low temperatures (550°C).
- The high pH in the pure biochars is increasing the pH in the soil when mixed.
- The initial content of DOC and P is governing the potential release of DOC and P from pure biochar.
- When biochar is mixed into the soil, the biochar-induced changes (e.g. pH and EC) will affect the potential release of DOC and P.
9 Release and transport of colloids, DOC and P

9.1 Introduction
The release and retention of different compounds in the soil, is a complicated mechanism governed by surface charge and other important soil properties (e.g. pH, EC).

The transport of contaminants in soils is mostly controlled by some main factors, including:

- The sorption on the soil surfaces
- The presence of carriers, that enhance the mobility of contaminants by sorption
- The transport pathways (or percolation patterns) (Kumari, 2015)

The use of biochar as a soil amendment is suggested to influence the water transport pattern and to increase the soil sorption capacity, due to its sorption affinity for contaminants and other organic compounds. The sorption ability of biochar has been attributed to the increased SSA, water holding capacity and cation and anion exchange capacity (Chintala et al., 2013). This chapter focuses on the effect of the NIMA biochar application to different soil types on the water transport and the leaching of colloids, DOC and P.

For that purpose, two different- scaled experiments were conducted:

1. The column leaching experiment, to examine the short term effect of NIMA biochar application (40 kg ha⁻¹) to intact soil columns on soil functions, such as water transport, and the leaching of DOC, colloids and P.
2. The field lysimeter leaching experiment, to investigate the effect of increasing concentrations of NIMA biochar on three different textured agricultural soils under conventional management conditions.

9.2 Methods

9.2.1 Column leaching experiment
The leaching experiment was performed on 20x20 cm undisturbed soil columns from the field in Jyndevad which were sampled from the top soil. Further treatment of the columns is shown in figure 50. A 5 cm high plastic ring was attached to the upper side of the column with duct tape, for further addition of an extra 5 cm layer of soil/soil-biochar. The control columns without biochar were filled with 2.4 kg air-dried, sieved (<2 mm) bulk soil from JYN and the columns with biochar were filled with a mixture of bulk soil and 23.7 % of biochar, corresponding to 40 kg/ha (see figure 49). The columns were weighed subsequently before the leaching experiment.
Before the leaching experiment, the columns were slowly saturated from the bottom with artificial soil water (0.652 mmol L$^{-1}$ NaCl, 0.025 mmol L$^{-1}$ KCl, 1.842 mmol L$^{-1}$ CaCl$_2$, and 0.255 mmol L$^{-1}$ MgCl$_2$) for 1 week, and then drained for 3 days at a matric potential of -10 cm at the bottom of the column.

The columns were then placed on 1 mm steel mesh under a rotating head, where irrigation was performed with 44 randomly placed needles to ensure a homogenous distribution of artificial rain water (0.012 mmol L$^{-1}$ CaCl$_2$, 0.015 mmol L$^{-1}$ MgCl$_2$, and 0.121 mmol L$^{-1}$ NaCl) on the soil surface. The artificial rain water was applied by a peristaltic pump with an intensity equaling 10 mm h$^{-1}$. The time when the first drop leached through the column was recorded and named as the water breakthrough time. When steady state was reached, the irrigation head was switched to another irrigation head containing water enriched with tritium (radioactive conservative tracer) which was applied for 10 minutes with the same intensity (10 mm h$^{-1}$) and resumed with artificial rain water. The columns were irrigated for 29 hours and the effluent was collected in plastic bottles, placed underneath the installation on a turning table, with sample intervals of 11x 10 min and 14x 120 min (figure 51).
The leachate fractions were analyzed for pH, EC, turbidity, DOC, total phosphorus (TP), total dissolved phosphorus (TDP) and tritium activity. The particulate phosphorus (PP) was calculated as the difference between TP and TDP. Turbidity was determined in nephelometric units on a Hach 2100AN turbidimeter. Tritium activity (decay per minute DPM) was measured on 1 mL of the outflow mixed with 2 mL ELGA water and 17 mL scintilations liquid, with a scintillation counter (TriCarb 2250 CA). TP and TDP were measured as described in section 8.2.2. After the leaching experiments, the columns were oven dried at 105 ° for 3 days and then weighed again to determine bulk density (Norgaard et al., 2013).

9.2.1.1 Statistical Analysis

In the Software Sigma Plot version 11, the significant effect of biochar amendment was determined using the Student’s t-test. At $p<0.05$, significant difference was accepted.

9.2.2 Lysimeter leaching experiment

The NIMA biochar from the producer Frichs A/S was tested as a soil amendment in an outdoor lysimeter experiment in Southern Denmark, which was implemented in June 2015.

9.2.2.1 Site description

The lysimeter setup is located in the Askov experimental station in Southern Jutland (55°28’N, 9°06’E), facilitating 124 lysimeter units.

9.2.2.2 Experimental setup

The lysimeter in Askov is a 150 cm deep, round polyester tank with a surface area of 0.83 m². In the bottom of the lysimeter a 25 cm layer of fine sand is acting as drainage, and the
remaining upper layer is filled with the experimental soil (figure 52). The rainwater flowing through the soil in the tank is collected in plastic bottles in an underground corridor, as shown in figure 52.

![Figure 52. Left; lysimeter set up. Right; underground corridor in Askov where the effluents are collected.](image)

In total, 48 lysimeters were packed with three different Danish agricultural soils, corresponding to 16 lysimeters per soil type. The plough layer (upper 20 cm) for every soil was mixed with 0, 0.5, 1 and 2 % Nima biochar \((n=4)\). The lysimeters were conventionally cultivated with ryegrass, and received nitrogen fertilization in July and August 2015. The effluents for the period 7/4/2015 – 12/30/2015 were collected in plastic bottles and stored in a freezer until laboratory measurements were conducted. The effluents were measured for pH, EC, DOC and TP as described in section 8.2.1-8.2.2. The turbidity on the effluents was measured in Nephelometric Turbidity units (NTU) on a Hach 2100 Turbidimeter. The precipitation data for Askov were collected on the agroecological meteorological database.

### 9.3 Results

#### 9.3.1 Biochar effect on transport pathways

The flow of water in a soil profile and thus the transport of solutes can occur as matrix flow or macropore flow. The matrix flow will allow the water and solutes to move vertically through and interact with the whole soil pore system, and thus trigger the mobilization of many contaminants. The macropore flow (or preferential flow) is the uneven and rapid movement of water and solutes, due to for example earthworm burrows, root holes or cracks.
Biochar incorporated into the soil, may result in altered percolation pathways and retention times by decreasing the bulk density and increasing the porosity of the soil. The physical structure (e.g., irregular shape, large particle size) of the biochar can change the pore size distribution of the soil and increase the water infiltration (Kumari, 2015).

The tritium that was used as an inert tracer to characterize the water transport through the soil columns was demonstrated in a tritium breakthrough curve (BTC), where the tritium concentration (C/C₀) was plotted against time (Appendix B). Kumari et al. (2015) stated that the shape of the tritium BTC is dependent on the bulk density of the investigated soil, and found, that decreasing bulk density after biochar application will reduce the peak concentration and result in longer time to the peak, due to slower movement of tritium in soils with lower bulk densities. The peak concentration and maximum peak time from the tritium BTC for the reference soils and the biochar-amended soils are stated in table 6. Both the average maximum peak time (p=0.039), and the peak concentration (p=0.003) in the biochar amended soil are statistically different form the reference soil, indicating a change in the transport pathways.

Table 6. Showing the 5 % arrival time and Max. peak concentration (h) and the peak concentration in C/C₀ for the Reference soil columns (blue) and the biochar amended soil columns (yellow).

<table>
<thead>
<tr>
<th></th>
<th>No biochar</th>
<th>With biochar</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Column 316</td>
<td>Column 044</td>
</tr>
<tr>
<td>5% arrival time</td>
<td>5.94</td>
<td>4.99</td>
</tr>
<tr>
<td></td>
<td>Column H9</td>
<td>Column 553</td>
</tr>
<tr>
<td>Max. peak time</td>
<td>9.5</td>
<td>7.5</td>
</tr>
<tr>
<td></td>
<td>Column H15</td>
<td>Column 124</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>9.5</td>
</tr>
<tr>
<td></td>
<td>Column 61</td>
<td>Column P169</td>
</tr>
<tr>
<td></td>
<td>9.5</td>
<td>5.71</td>
</tr>
</tbody>
</table>

There was no significant difference for the 5 % arrival time that was found from the mass accumulated tritium curves. The 5 % arrival time is the time it takes for 5 % of the tritium to leach out (Norgaard et al., 2013).

9.3.2 Biochar effect on contaminant carriers
Small particles, with sizes ranging from 1 nm to 10 µm in diameter, are referred to as colloids. The group of colloids in the soil includes clay minerals, Fe and Al compounds, macromolecules, and bio- colloids (bacteria and viruses) (de Jonge et al., 2004). Due to their small sizes, colloids have characteristically higher specific surface areas with a high negative surface charge, which makes them highly reactive in the subsurface soil (de Jonge et al.,
2004). Hence, colloids have the potential to adsorb and carry nutrients and potential contaminants with low solubility into the soil profile, and eventually into the groundwater.

**Sources and mobility of colloids**

The main source of mobile colloids is the *in situ* mobilization of particles that are naturally present in the soil. This particle release mainly occurs because of changes in the solution chemistry, where the release is favored by high pH, high Na⁺ saturation and low ionic strength (Kretzschmar et al., 1999).

The mobility of colloids is affected by the pore water chemistry, such as ionic strength and pH (Grolimund and Borkovec, 1999) and physical properties, including pore size distribution and pore geometry and continuity (Bradford et al., 2009). The colloid-facilitated transport takes place when, 1) colloids are present, 2) the contaminants or nutrients sorb to the colloids and 3) the colloids (with the sorbed contaminants) are transported through the soil profile (Kretschmar et al., 1999). Likewise, the stability of dispersed colloids in the solution is governed by the surface potential of the colloid, and the ionic strength and pH in the solution (Kumari, 2015).

Biochar has the potential to modify the colloid-facilitated transport in different ways, when incorporated into the soil. First, colloidal-sized biochar particles may sorb contaminants and thus transport contaminants through the soil profile, however less is known about the transport of biochar particles from the site of application (Wang et al., 2013). Zhang et al. (2010) found that the transport of biochar particles (<70µm) in a sand column was reduced at lower pH and high ionic strength and increasing particle sizes. Secondly, the biochar will indirectly influence the mobility and stability of colloids by altering the soil properties and structure. This is mainly due to the ability of biochar to increase the soil pH that results in deprotonation of charged sites on soil minerals and organic material.

**9.3.3 Biochar effect on leachate chemistry**

**Column leaching experiment**

The pH in the biochar-amended soils (ranging from pH 6.8-7.3) was slightly higher, compared to the reference soil (ranging from pH 5.6-7) (figure 53). This observation is in agreement with other leachate pH results by, for example Bradley et al. (2015) who found statistically significant increased leachate pH in wood biochar (up to 5 wt %) amended sandy soil.

The EC values peaked at around 7 hours after the start of the experiment, suggesting a matrix flow of water and solutes through the columns (figure 53). After approximately 15
hours, the EC in the effluents is decreasing towards a steady value ranging from 0.04 to 0.2 mS cm\(^{-1}\). The EC was generally higher in the biochar amended soil columns. The higher EC in the biochar amended soils, does not correspond with the findings of Kumari et al. (2014) who found a decrease in EC in biochar amended soil columns.

Figure 53. Left; Outflow plotted against pH, right; outflow plotted against EC, for reference and biochar amended soil.

Lysimeter leaching experiment

The increasing NIMA biochar application showed no influence on the pH in the lysimeter experiment. In this experiment, the pH might more likely be governed by the soil type and the precipitation pattern (Appendix C). The results for the EC from the lysimeter experiment illustrates, that the increasing biochar concentration had a clear effect in the sandy LUN soil, where the EC in the effluents increased after approximately one month, with the highest effect in the 2 % NIMA application.

In the ASK and STEN soils, the NIMA is also influencing the EC, but the effect appears later compared to the LUN soil, and only to a minor degree in the examined period. The transmission of water through the soil is one explanation for the higher EC in the sandy soil, since the large pores, and certainly also the occurring matrix flow, will allow the water to be distributed in the whole soil matrix, and adsorb many salts and ions on its way through the profile. The increasing EC in the LUN soil with 2 % NIMA peaks after two month and decreases rapidly after that (Appendix D).

Biochar effect on DOC

Column leaching experiment

The biochar- amended columns showed significantly higher values of DOC in the effluent, especially after approximately 110 mm outflow (see figure 54).
The higher DOC concentration in the leachate is mainly caused by the initial content of DOC in the biochar and the biochar-induced changes, such as pH and EC.

**Lysimeter leaching experiment**

The DOC concentration in the effluents collected from the lysimeter experiment were similar and consistent in the LUN and STEN soil, ranging from approximately 1 to 10 mg L$^{-1}$, indicating no effect from the increasing biochar concentration (see appendix F). Sandy soils are observed to have low abilities to retain organic material (Józefaciuk et al., 1996), therefore one would assume that the application of biochar might increase the release of DOC, due to the initial DOC content of biochar. However, this is not the case in the lysimeter experiment, probably because of the biochar used (NIMA) which had a relatively low potential release of DOC (measured in the batch experiment) and because of the low application dosage.

In the ASK soil with a high initial content of humus, the increasing biochar concentration seem to suppress the release of DOC. This assumption is based on the observed peak in the unamended ASK soil on the 11/18/2015 with an average DOC concentration of 41.22 mg L$^{-1}$ compared to the average DOC concentration for the 2 % NIMA amended ASK soil on the same date, accounting for 9.59 mg L$^{-1}$ (see figure 55).

The peaks on the 11/18/2015 may indicate a period of heavy rainfall, with fast transport of water and solubles through the soil in the lysimeters.
Biochar effect on the leaching of colloids

Column leaching experiment

As for the DOC, also the leaching of the colloidal fraction may be influenced by the application of biochar, as the transport of colloids is highly dependent on soil pH and EC (Zhang et al., 2010). The application of biochar increased the turbidity in the effluents (measured in NTU), indicating higher leaching of colloids. Moreover, figure 56 illustrates the variability among the four biochar-amended replicates compared to the four replicates without biochar. The higher turbidity may be caused by the colloidal biochar fraction, and by the changes in the pH and the increasing release of DOC (Bolan et al., 2011).
Lysimeter leaching experiment

The increasing biochar application had no effect on the turbidity in the effluents of the lysimeters. The Clayey STEN soil had the highest turbidity with much variation among the replicates (Appendix E).

9.3.4 Biochar effect on P leaching

The leaching of phosphorus in soils has been recognized as an important pathway of P losses to aquatic areas (de Jonge et al., 2004) contributing to the eutrophication of surface waters (Wang et al., 2016).

Important transport mechanisms for the P leaching in soils are the dissolved P that can be transported via the soil matrix and with preferential flow, and the colloid-facilitated transport (particulate P) (Verheyen et al., 2015).

The application of biochar is suggested to decrease nutrient leaching under different soil conditions, mainly related to the increased reactive surface area (Verheijen et al., 2010), and the biochar induced changes in pH and EC (Dari et al., 2016).

The mostly inconsistent results from studies regarding the effect of biochar on P and whether biochar enhances P sorption or P release underlines the variability among the biomass used and the production process (Dari et al., 2016).
Column leaching experiment

The PP and TDP for the biochar amended and reference soils are plotted against the outflow, and illustrated in figure 57.

The accumulated PP in figure 57 indicates generally higher PP in the biochar-amended soils compared to the reference (with few exceptions).

Figure 57. PP and TDP and accumulated PP and TDP in biochar amended and reference soils, obtained by the column leaching experiment.

The changes in the soil (increase of surface area and decrease in exchange capacity of the surface functional groups) that result from the application of biochar influence the sorption and desorption of P. Biochar mixed into mineral soil, may result in P sorption competition between the sorption complex of soil and that of biochar (Morales et al., 2013).

Many studies, concerning the effect of biochar on P leaching, show the diversity in P chemistry in the soil after biochar application. As for instance, Morales et al. (2013) who found P sorption and desorption capacities in different biochar obtained by different Amazonian tree species under different formation processes. Soinne et al. (2013) investigated the effect of biochar obtained by a mixture of Norway spruce and Scots pine, on a sandy and a clayey soil. They found that the biochar used, had no affinity to sorb P and may therefore not directly influence the sorption in soils, however, the biochar-induced changes (increase in soil pH) may improve the availability of P in soils.
The increasing trend in TDP (figure 57) in the biochar amended soils, may be caused by the biochar induced changes in pH that is enhancing the availability of P. The late occurrence of the rise in TDP (approximately between 100 and 150 mm outflow) may also indicate that the initial P content in the biochar takes longer time to be dissolved and transported.

**Lysimeter leaching experiment**

The highest P concentrations in the effluents and variation among the replicates was found in the Clayey STEN soil (Appendix G). This is in accordance with the highest turbidity in the STEN soil, indicating some colloid facilitated transport of P by the clay particles. This is further illustrated in figure 58, where the turbidity is plotted against the P concentration in the effluents is most significant in the STEN soil.

![Figure 58. Turbidity (NTU) plotted against the P concentration in the effluents of the different soil types (LUN, ASK, STEN) with different NIMA biochar applications (different colors).](image)

However, there was no effect from the increasing biochar concentration.

**Sub- conclusion**

- The application of biochar showed statistically difference (p=0.003) between the peak concentration of tritium in the biochar amended and reference soil, indicting biochar induced changes in the water transport through the soil columns
- The pH and EC was higher in the biochar amended soils columns in the column leaching experiment. For the lysimeter leaching experiment only the sandy LUN soil experienced a rise in EC with increasing biochar application.
- The initial content of DOC and the biochar induced changes caused higher concentrations of DOC in the leachate of the column leaching experiment. For the lysimeter leaching experiment, the increasing biochar application seemed to suppress the leaching of DOC.
The application of biochar slightly increased the turbidity and P concentration in the leachate of the column leaching experiment. There was no effect of biochar application in the lysimeter leaching experiment.
10 Conclusions
The purpose of this thesis was to investigate the influence of biochar on the behavior of soil and various soil characteristics when incorporated into different textured agricultural soils.

- The different biochars had different physical and chemical properties, there was a difference between the biochars produced at different temperatures for the content of nutrients (C and P) and for the SSA (ranging from ranging from 214 to 411 m² g⁻¹).
- The NIMA biochar had the highest total porosity.
- The application of biochar in the concentrations 0, 0.5, 1 and 2 % to the three different textured soils (sandy to clayey) resulted in lower bulk densities (the highest biochar application concentration accounting for the lowest bulk density). The high initial porosity in all biochars increased the total porosity in all soils. Overall the NIMA biochar induced the most significant changes in all soils.
- The changes in soil characteristics (SSA, bulk density, total porosity) induced by the biochar application, influenced the soil hydraulic properties.
- The soil water retention in all soils was highest with 2 % biochar application. The application of the NIMA biochar resulted in highest water retention in all soils.
- The gas transport parameters ($k_a$ and $D_p/D_o$) are highly influenced by the air filled porosity ($\varepsilon$).
- At pF 2.7, the increasing application of all biochars increased the $D_p/D_o$ in the ASK soil.
- The biochar induced changes in soils (increasing pH and EC) may affect the sorption and desorption of DOC and P.
- In general, the soil type was governing important processes, since the maximum application of 2% biochar may only have a small effect.
- Different biochars showed diverse behaviors in different soil types.
11 Perspectives and future considerations

The use of biochar in agriculture has recently been considered as an obvious solution, that when incorporated to the soil can combat climate change and simultaneously contribute to the improvement of degraded land (Ding et al., 2016). Biochar can be produced from all types of biomass and with different temperatures and durations, whereby the starting materials can vary greatly – and hence the results obtained.

Based on the different characteristics of biochars, and their different behaviors in various textured soils, it can be assumed that one can govern the behavior of the biochar in the soil. However, the type of biochar must be picked based on the specific objective. This thesis and recent studies illustrate the immense variability in biochar characteristics and their different behaviors in different textured soils. Especially the differences among biochars obtained at different production temperatures needs more attention.

Taking into account that this study found larger SSA on biochars obtained at 550°C compared to the ones obtained at 700°C, there is a need to evaluate the influence of biochars obtained at different temperatures on the soil water retention. The larger SSA may be able to retain even more water.

The column leaching experiment, that was carried out with and without biochar application, needs to be done on pure biochar columns, to determine the potential of pure biochar for P and colloid leaching. Clearly, not all questions regarding biochar are clarified yet. In particular, it is important to ensure that the use of biochar remains affordable and that all possible negative impacts on soil functions can be excluded and that the chosen biochar actually will have a positive effect in the soil. Some few negative effects might be:

- Contaminants that are present in some biochars (PAH, heavy metals, dioxins) may influence important soil functions. Less is known about the short and long term effects of PAH (Verheijen et al., 2010)

- Too high amounts of biochar application (<67 t ha⁻¹) can have negative effects on earthworm populations, due to high pH values and salt concentrations
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Figure 59. The air filled porosity ($\varepsilon$) plotted against and the $k_a$ at pH 1.5, 2, and 2.7 soil biochar mixtures, different colors indicate biochar application rate.
Figure 60. Tritium Breakthrough curve for reference (black) and biochar amended (red) soils.
Figure 61. pH (black line) obtained from the lysimeter leaching facility in Askov (Southern Jutland) in the period 7/1/2015 – 12/31/2016 for all soils (LUN, ASK, STEN) with application of NIMA biochar in the concentrations 0, 0.5, 1 and 2 %. The blue lines are representing the precipitation data and the vertical dashed red lines the nitrogen fertilizer application.
Figure 62. EC values (black line) obtained from the lysimeter leaching facility in Askov (Southern Jutland) in the period 7/1/2015 – 12/31/2016 for all soils (LUN, ASK, STEN) with application of NIMA biochar in the concentrations 0, 0.5, 1 and 2%.
The blue lines are representing the precipitation data and the vertical dashed red lines the nitrogen fertilizer application.
Figure 63. Turbidity (NTU) (black line) obtained from the lysimeter leaching facility in Askov (Southern Jutland) in the period 7/1/2015 – 12/31/2016 for all soils (LUN, ASK, STEN) with application of NIMA biochar in the concentrations 0, 0.5, 1 and 2%. The blue lines are representing the precipitation data and the vertical dashed red lines the nitrogen fertilizer application.
Figure 64. DOC concentrations (black line) obtained from the lysimeter leaching facility in Askov (Southern Jutland) in the period 7/1/2015 – 12/31/2016 for all soils (LUN, ASK, STEN) with application of NIMA biochar in the concentrations 0, 0.5, 1 and 2%. The blue lines are representing the precipitation data and the vertical dashed red lines the nitrogen fertilizer application.
Figure 65. P concentrations (black line) obtained from the lysimeter leaching facility in Askov (Southern Jutland) in the period 7/1/2015 – 12/31/2016 for all soils (LUN, ASK, STEN) with application of NIMA biochar in the concentrations 0, 0.5, 1 and 2 %. The blue lines are representing the precipitation data and the vertical dashed red lines the nitrogen fertilizer application.