Faculty of Agriculture and Forestry
University of Helsinki

WOOD-DERIVED SOIL AMENDMENTS AND THEIR EFFECTS ON SOIL FERTILITY AND GREENHOUSE GAS EMISSIONS FROM CULTIVATED BOREAL SOILS

Kenneth Peltokangas

DOCTORAL DISSERTATION

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ABSTRACT

Ligneous, i.e., wood-derived soil amendments are an abundant source of recalcitrant carbon that could be used to improve and maintain soil fertility as well as to mitigate climate change. However, there is still much to be learned about the mechanisms that determine the specific effects of different types of ligneous soil amendments. Furthermore, little research has been conducted on fine-textured boreal clay soils, which is one of the dominant soil types in northern agriculture.

The purpose of this study was to investigate how pulp sludge and biochar materials affect soil properties and greenhouse gas emissions in the long-term. Our main hypothesis was that ligneous soil amendments can increase soil organic carbon content for the long-term due to the persistent nature of lignocellulose and aromatic biochar and subsequently improve soil structure, water retention and microbial processes involved in soil greenhouse gas exchange. Our findings showed that most of the ligneous soil amendments increased soil organic carbon content, however, the effects on soil bulk density and total porosity were limited. Soil carbon dioxide emissions were mostly unchanged by the amendments, and the impact on nitrous oxide emissions was inconclusive. Nevertheless, the greenhouse gas data collected during laboratory and field experiments indicated that the ligneous soil amendments were able to alter the temporal dynamics of greenhouse gas emissions, likely due to their effect on soil pH and soil moisture.

We also found that most of the studied biochars had the capacity to retain mineral nitrogen for extended periods of time. However, we observed significant differences in how nitrate was retained among the various biochars, which was attributed to differences in their porosity and hydrophobicity. Our findings indicate that biochar has the potential to retain a substantial amount of residual nitrate after harvest. These results have significant implications for measuring mineral nitrogen in biochar-amended soils, as the conventional method for extracting mineral nitrogen may substantially underestimate the total amount of mineral nitrogen in the amended soils.

Ligneous soil amendments are a viable option for adding long-lasting carbon to soil, which can help increase soil pH and improve soil structure. However, the effects on boreal clay soils are limited because of the already high fertility of these soils.

CONTENTS

LIST OF ORIGINAL PUBLICATIONS

This dissertation is based on the following four publications, which are referred to in the text by their roman numerals:

I **Peltokangas, K.**, Subin, K., Huusko, K., Havisalmi, J., Heinonsalo, J., Karhu, K., Kulmala, L. and Pihlatie, M. 2023 (accepted for publication). Ligneous amendments increase soil organic carbon content in fine-textured boreal soils and modulates N_2O emissions. PLOS ONE.

II Kulmala, L., **Peltokangas, K.**, Heinonsalo, J., Pihlatie, M., Laurila, T., Liski, J. and Lohila, A. 2022. Effects of biochar and ligneous soil amendments on greenhouse gas exchange during extremely dry growing season in a Finnish cropland. Frontiers in Sustainable Food Systems. p.414.
https://doi.org/10.3389/fsufs.2022.951518

III Kalu, S., Kulmala, L., Zrim, J., **Peltokangas, K.**, Tammeorg, P., Rasa, K., Kitzler, B., Pihlatie, M. and Karhu, K. 2022. Potential of biochar to reduce greenhouse gas emissions and increase nitrogen use efficiency in boreal arable soils in the long-term. Frontiers in Environmental Science.
https://doi.org/10.3389/fenvs.2022.914766

IV **Peltokangas, K.**, Pitkänen, N., Kanerva, S. and Pihlatie, M. 2023. Release, retention, and availability – towards mechanistic understanding of nitrogen retention by biochar. Finnish Meteorological Institute's Climate Bulletin Research Letters, 5.
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The aforementioned original articles are printed in this thesis synthesis with the permission of the original publishers.

Additional material
This thesis also contains some previously unpublished material on the effects of organic soil amendments on soil properties and GHG exchange.

CONTRIBUTIONS OF THE AUTHORS

I The experimental design and the subsequent manuscript were developed by KP. MP, JHe, KK, LK, and KH contributed to the planning and writing phases of the manuscript. Soil sampling and the subsequent laboratory work were carried out by KP and JHa. The mineral nitrogen and microbial biomass were determined by SuK and KP.

II The manuscript was written LK and KP while JHe, MP, TL, JL and AL contributed to the project during the development of the research plan and securing funding, as well as contributing to the later versions of the article. LK with the assistance of seasonal workers, performed the gas and vegetation sampling, while KP was responsible for analyzing the soil water retention properties.

III SuK and KK designed the study, while PT, KR, and LK maintained the field experiments at Qvidja. Gas sampling was conducted by JZ, LK, and SuK, while MP was responsible for analyzing the gas samples. Soil mineral nitrogen and microbial biomass analysis were performed by SuK and KP. BK analyzed the nitrogen leaching. SuK wrote the first draft of the manuscript while all of the authors contributed to the final article. This article was previously included in SuK's PhD dissertation.

IV KP was in charge of the manuscript and designing the experiment, while NP, SaK, and MP contributed to the final version of the manuscript. NP and KP conducted the growth experiment and analyzed the plant samples, while NP was responsible for the sequential extractions.

Additional material. Kenneth Peltokangas was solely responsible for all of the additional material.

AL: Annalea Lohila, BK: Barbara Kitzler, JHa: Jimi Havisalmi, JHe: Jussi Heinonsalo, JL: Jari Liski, JZ: Jure Zrim, KH: Karoliina Huusko, KK: Kristiina Karhu, KP: Kenneth Peltokangas, LK: Liisa Kulmala, MP: Mari Pihlatie, NP: Nelli Pitkänen, SaK: Sanna Kanerva, SuK: Subin Kalu, PT: Priit Tammeorg, TL: Tuomas Laurila.

LIST OF CHEMICAL ELEMENTS AND COMPOUNDS

C	Carbon
O	Oxygen
N	Nitrogen
P	Phosphorus
S	Sulphur
Al	Aluminum
Fe	Iron
Mn	Manganese
Zn	Zinc
K (K^+)	Potassium (ion)
Ca (Ca^{2+})	Calcium (ion)
Mg (Mg^{2+})	Magnesium (ion)
H^+	Hydrogen (ion) i.e. proton
NH_4^+ and NH_4^+-N	Ammonium (ion) and ammonium-nitrogen
NO_3^- and NO_3^--N	Nitrate (ion) and nitrate-nitrogen
NO_2^-	Nitrite (ion)
NO	Nitric oxide (gas)
N_2O	Nitrous oxide (gas)
N_2	Nitrogen (gas)
HPO_4^{2-}, $H_2PO_4^{3-}$	Phosphate (most common species in soil)
CO_2	Carbon dioxide (gas)
CO_3^{2-}	Carbonate (ion)
H_2CO_3, HCO_3^-	Carbonic acid, bicarbonate
$CaCO_3$	Calcium carbonate, calcite, limestone
O_2	Oxygen (gas)
CH_4	Methane (gas)

LIST OF KEY CONCEPTS AND ABBREVIATIONS

Soil organic matter (SOM)	Soil Organic Matter refers to the organic fraction of the soil matrix formed from plant and animal residues in different stages of decomposition. Overall, SOM contains approximately 50% organic carbon (Pribyl 2010, Powlson et al. 2011a), especially in the surface soil (Broadbent 1953) (page 8).
Organic carbon (OC)	Organic Carbon refers to carbon that is bound to at least one hydrogen-atom and makes up the chemical structures of plant- and animal-derived compounds. In this dissertation, OC is often used to distinguish amendment-derived carbon from native soil organic carbon, which is referred to as soil organic matter or SOM (page 8).
Soil or soil matrix	Soil matrix refers to the solid part of soil that makes up the majority of its volume. It includes mineral particles, organic matter, and other soil constituents. The size, shape, and arrangement of soil particles affect how well the soil retains water, nutrients, and air, and how easy it is for plant roots to penetrate the soil. See 1.1.1 Soil as physical habitat for plants and microorganisms (page 9).
Organic soil amendments	Organic soil amendments are substances that can be added to soil to enhance its physical and chemical properties. These materials can come from a variety of sources, such as decomposed plant or animal materials, compost, biochar, and other organic waste products (page 19).
Ligneous	Meaning 'wood-derived' referring to something consisting of woody materials, i.e., cellulose, hemicellulose and lignin. See 1.3 Wood-derived soil amendments and their use in agriculture (page 20).

Pulp sludge	Waste biomass generated during the making of pulp and paper. It is mixture of water, wood fibers and chemicals, but the exact composition varies between paper mills and between various types of pulp sludge. See 1.3.1 Production and properties of pulp sludge (page 21).
Biochar	is a type of charcoal that is made with the deliberate intent to be used as soil amendment. It is produced by heating organic materials, such as wood, in the absence of oxygen, which results in a porous and carbon-rich substance. See 1.3.3 Production and properties of biochar (page 24).

PAW	**Plant Available Water**, which refers to water content retained in soil between the point field capacity (Ø=10 μm, i.e., pF 1.8) and permanent wilting point (Ø=0.2 μm, i.e., pF 4.2).
WHC	**Water Holding Capacity**, referring to the maximum amount of water retained by soil after gravitational water has been allowed to drain away.
WFPS	**Water Filled Pore Space**, referring to the proportion of the total pore volume filled with water.
GHG	**Greenhouse Gas**, and referring to the volatile compounds, which contribute to the global greenhouse effect. In this dissertation, the term refers exclusively to CO_2, N_2O and CH_4.
SSA	**Specific Surface Area**, referring to the total surface area of soil particles, including the area of internal pores.
CEC	**Cation Exchange Capacity**, referring to the capacity for soil to retain positively charged ions.
BD	**Bulk Density**, referring to the ratio of soil mass divided by total soil volume including voids between soil particles.

1 INTRODUCTION

The largest terrestrial carbon (C) pool is found in soils, which holds about ~1 500 Pg C up to a depth of one meter (Eswaran et al. 2000, Jobbágy & Jackson 2000, Batjes 1996, 2014, Köchy et al. 2015). More than half (~55%) of this C pool is located in the top 0.3 m layer of soil (Lal 2018), consisting mostly of dead animal and plant residues and organic compounds in varying stages of decomposition (Lehmann & Kleber 2015). This C pool is called **soil organic matter** (SOM) and is crucial for soil health, as it contributes to its physical structure, nutrient and water retention (Minasny & McBratney 2018), as well as its ability to resist acidification (Hartikainen 1985). However, in conventional agriculture, C and nutrients are harvested along with crops and are also lost due to increased decomposition, leaching, and erosion. Furthermore, the SOM pool is often left unreplenished due to limited inputs of fresh **organic carbon** (OC) into the soil (Powlson et al. 2011b, Amundson et al. 2015). This trend along with perpetual intensification of agriculture since the 1960s has led to a significant decline in SOM content in cultivated soils (e.g., Lal 1999, Houghton 2008, Heikkinen et al. 2013, Steinmann 2016, Anderson & Rivera-Ferre 2021), which threatens both soil fertility (Stavi & Lal 2013) and contributes to climate change (Lal et al. 2007).

As a consequence of climate change, there is a growing interest in sequestering C back into the soil (Poulton et al. 2018, Smith et al. 2020). This could be achieved through the use of external waste biomasses such as manure, composts, biochars, or pulp sludges. These carbon-rich biomasses are collectively known as organic soil amendments, and they are considered natural options for C sequestration while also providing a way to recycle nutrients back into primary production (Lal 2010, Larney & Angers 2012, Sanderman et al. 2017). Furthermore, the C sequestration paradigm suggests that we can convert cultivated soils from C sources into sinks and improve their fertility (Thangarajan et al. 2013) by controlling the quantity and quality of OC applied to the soil (Paustian et al. 2016). However, our current understanding of soil C and nitrogen (N) cycles is insufficient to predict the full impact of organic amendments on soil fertility and greenhouse gas (GHG) exchange (Jeffery et al. 2011, Cayuela et al. 2014, Faubert et al. 2016, Malik et al. 2018). Therefore, further research is necessary to better comprehend the soil interactions that determine the environmental effects of soil amendments and to establish sustainable farming practices (Smith 2012, Paustian et al. 2019).

1.1 THE IMPORTANCE OF SOIL ORGANIC CARBON TO SOIL FERTILITY

Sustainable agriculture aims to maintain and improve soil fertility (Lal 2008, Pretty 2008, Bruinsma 2017). Soil fertility refers to soil properties that promote biological productivity by ensuring adequate air, water, and nutrient availability for plant production. Although the concepts of soil fertility and soil health are

somewhat ambiguous (Pankhurst et al. 1997), SOM content is commonly used as an indicator for soil fertility because of its ability to provide both nutrients and energy to microorganisms as well as increasing soil water and nutrient retention (Lal 1997, Powlson et al. 2011c). Indeed, the importance of frequent OC inputs into the soil and adequate SOM content cannot be overstated in the context of soil ecosystems making them appealing choices for improving soil fertility.

Organic soil amendments often contain both easily decomposable organic compounds, which provide C and energy for the soil system and encourage soil aggregation through microbial secreted mucilage, as well as more stable C fractions that are associated with water and nutrient retention (Hartikainen 1985). However, the application of external OC and nutrients into the soil system may also cause undesirable effects (Janzen 2006), such as the decomposition of native SOM through positive priming (Fang et al. 2015, Guenet et al. 2018, Kok et al 2022), nutrient immobilization by microorganisms (Marzi et al. 2020, van der Sloot et al. 2022), or increased production of GHGs through aerobic and anaerobic soil respiration (Thies & Grossman 2006, Paul 2014). Therefore, it is crucial to understand the mechanisms that govern soil interactions and how soil amendments contribute to different aspects of soil fertility.

1.1.1 SOIL AS PHYSICAL HABITAT FOR PLANTS AND MICROORGANISMS

Soil has a porous matrix composed of mineral particles of varying sizes and minerology, as well as SOM originating from dead plant and animal debris, and recycled organic waste materials. These materials undergo continuous physical and chemical changes, leading to the formation of distinctive soil layers known as horizons (**Fig 1**). At the soil surface, partially decomposed OC residues make up the organic layer (O horizon), and the underlying soil (A horizon) is often darkened by the accumulated SOM. In agricultural soils, the boundary between the topsoil and the lighter subsoil (B horizon) is frequently visible, as plowing mixes the upper 10–25 cm of the soil profile, creating a distinct organically enriched plow-layer where most plant roots are located. Furthermore, plowing can also disrupt blocky and prismatic soil structures, resulting in a more granular structure where aggregates of varying size and shape dominate (Weil & Brady 2017, **Fig 1**).

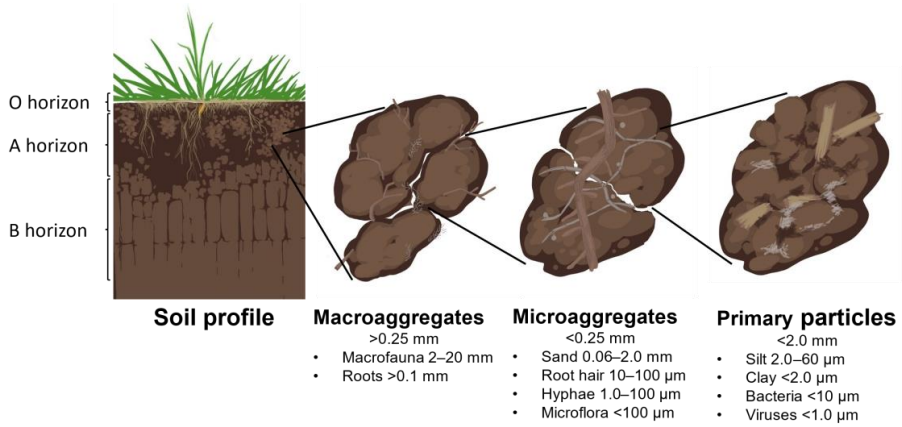

Figure 1 Soil matrix consists of mineral particles and SOM in different orders of structure. At the general level, soil profile is divided into organic litter layer (O horizon), organically rich top soil (A horizon), lighter subsoil (B horizon), and underlying parent material. The soil structure of the top soil is often dominated by micro- and macroaggregates while the subsoil may have larger blocky or prismatic structures (modified from Weil & Brady 2017).

Soil aggregates are composed of individual soil particles that are categorized into different textural classes based on their size (**Table 1**). Their size being one of the determining factors for properties, such as specific surface area (SSA) and cation exchange capacity (CEC), which generally increases as their size decreases. Furthermore, clay particles are formed from stacked mineral sheets that often have inter layer surfaces, providing additional surface area that contributes to their high CEC (McBride 1994). In comparison, SOM consists of organic residues arranged in a more or less amorphous manner, with large SSA and numerous functional groups that contribute to CEC. Consequently, soils that are rich in both SOM and fine textured mineral matter (silt and clay) are typically fertile, whereas coarse-textured soils and soils with low SOM content lack the necessary properties to retain nutrients and water, and would therefore benefit most from OC (Blanco-Canqui 2017, Atkinson 2018, Minasny & McBratney 2018).

Table 1 Classification of soil particles according to their size based on the systems used by United States Department of Agriculture (USDA) and International Society of Soil Science (ISSS) as well as the Finnish Geotechnical system. The values for specific surface area (SSA), cation exchange capacity (CEC), bulk density (BD), and porosity are based on Korhonen (1974), Rantamäki (1982), and Blume et al. (2010).

Textural classes		**Particle size range**				**SSA**	**CEC**	**BD**	**Porosity**
		USDA (mm)	**ISSS (mm)**	**Geotechnical**		**($m^2 g^{-1}$)**	**(cmol(+) kg^{-1} at pH 7)**	**($g\ cm^{-3}$)**	**(%)**
Gravel		>2.0	>2.0	Sr	>2.0	<0.1	<10	1.16–1.70	33-50
Sand	Very coarse	1.0–2.0	0.2–2.0	KHk	0.6–2.0	<1.0	<20	1.17–1.63	44-50
	Coarse	0.50–1.0		HHk	0.2–0.6				
	Medium	0.25–0.50		KHt	0.02–0.06	0.1–1.0			38-50
	Fine	0.10–0.25		HHt	0.02–0.06				
	Very fine	0.05–0.10	0.02–0.2	KHs	0.006–0.02				41-55
Silt		0.002–0.05	0.002–0.02	HHs	0.002–0.006				
Clay		<0.002	<0.002	S	<0.002	25–750	>40	0.93–1.72	35–65
Organic matter					0.054–2.0	500–800	200–400	~0.5	89-94

Bulk density (BD) is a common descriptor for the spatial arrangement of soil particles (**Fig 2**). Therefore, when comparing soils, a decrease in BD indicates a reduction in soil mass and an increase in the volume of pores, which can have a positive influence on soil fertility through improved water flow and aeration (Assouline & Or 2013). Conversely, increased BD implies compaction (**Fig 2**), which is often linked to increased surface runoff, erosion, poor root growth and nutrient uptake (Weil & Brady 2017).

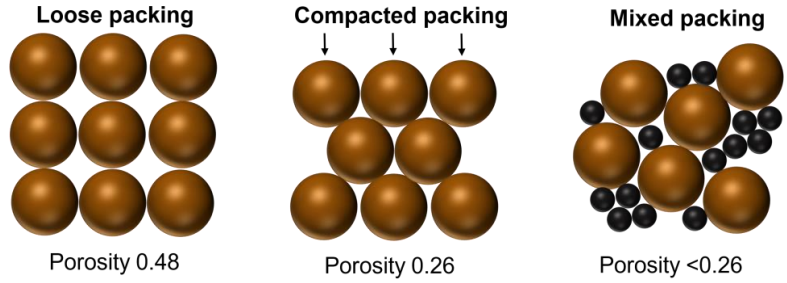

Figure 2 Loosely packed soil particles (monosized) lead to large pore volume while soil compaction leads to tightly packed particles and small pore volume. However, soils are often formed from various sized particles, which means that their porosity may be less than optimal (modified from Hillel 2013 and Robinson et al. 2022).

Because of their irregular shape and size, organic particles have generally very loose packing (**Fig 2**), which often increases soil porosity and therefore reduces BD. However, the lower density of OC relative to mineral matter means that the

soil BD can be reduced merely through the dilution effect of mixing lighter organic particles with heavier mineral matter (Robinson et al. 2022). In such cases, the reduced BD does not directly indicate improved soil structure or increased soil porosity. Soil organic amendments and other biomasses consist mainly of OC and have generally been found to reduce BD (e.g. Heuscher et al. 2005, Ruehlmann & Körsshens 2009). However, it is often unclear whether this is due to mixing of heavier mineral soil with lighter OC (Robinson et al. 2022), or because of improved soil structure. Consequently, it is often uncertain whether the application of soil amendments has positively impacted soil physical properties such as total porosity, aeration, water retention, and ultimately soil fertility (e.g. Minasny & McBratney 2018).

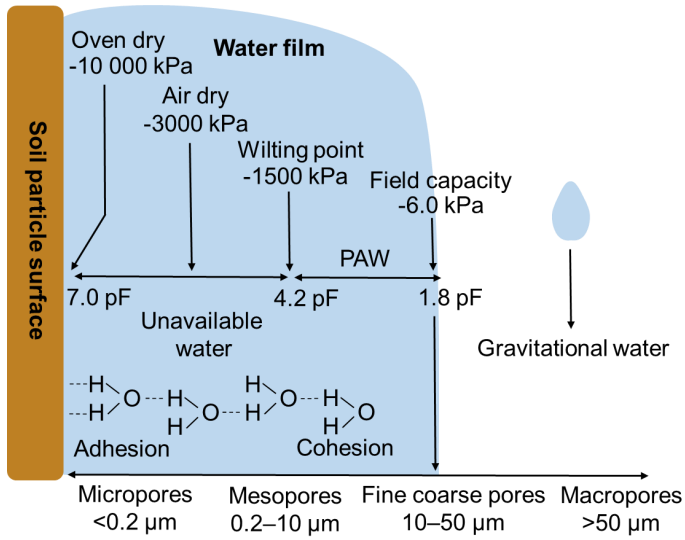

Figure 3 Conceptual representation of soil moisture: above field capacity (pF>4.2), water drains by gravity allowing **Macropores** (>50 µm) to transmit air through the soil. Finer pores (10–50 µm) retain most of the water that is available for plants (PAW) and transmit it via capillary action (adhesion and cohesion). **Mesopores** (0.2–10 µm) function as habitat for soil fauna while **Micropores** (<0.2 µm) adsorb water, nutrients, and gases that are mostly unavailable for organisms (modified from Blume et al. 2010).

Soil porosity and water holding capacity (WHC) are related through capillary action (adhesion and cohesion), which is influenced by the size and shape of soil pores (Hillel 2013, Weil & Brady 2017). Therefore, the total volume of soil pores is usually subdivided into various pore size categories according to their characteristics and functions (**Fig 3**). In this synthesis soil pores are categorized according to their influence on soil water regime (Blume et al. 2010). **Macropores** (Ø>50 µm) are usually found between soil peds and aggregates. The largest macropores (coarse pores) are large enough to accommodate plant roots while even smallest of the (fine) coarse pores are important for soil aeration and water flow. **Mesopores** retain water after drainage and contain most of the plant available water (PAW). The range of mesopores is linked to the drainage boundaries between field capacity (Ø=10 µm, i.e., pF 1.8) and permanent wilting point

(Ø=0.2 µm, i.e., pF 4.2). The importance of macro- and mesopores lies in their ability to facilitate water and gas flow, which is directly related to the fourth power of the radius of the pores (Weil & Brady 2017). As a result, it is mainly the larger pores that affect the ratio of air-to-water-filled pores, which affects the concentrations of carbon dioxide (CO_2) and oxygen (O_2), and ultimately determining whether soil conditions are aerobic or anaerobic.

In clay soils, **Micropores** (Ø<0.2 µm) dominate the total pore volume, which results in high WHC, but often leads to inadequate aeration due to a lack of larger soil pores (Troeh & Thompson 2005, Rochette et al. 2008). As a results, clay soils suffer periodically from anaerobic conditions, which produce nitric oxide (NO), nitrous oxide (N_2O), nitrogen gas (N_2), hydrogen sulfide (H_2S) and methane (CH_4) through microbial activity. Sandy soils, on the other hand, are dominated by larger soil pores that are formed between the coarser soil particles. These have small SSA and contribute little to water and nutrient retention (Troeh & Thompson 2005). However, the abundance of large pores ensures that aerobic conditions predominate, and the main products of soil respiration are water (H_2O) and CO_2.

Due to its high SSA, amorphous and irregular shape, SOM has been suggested to address these weaknesses by increasing soil porosity and aeration in clay soils and improving water and nutrient retention in sandy soils (Troeh & Thompson 2005). Consequently, SOM and organic soil amendments are considered to mitigate the physico-chemical constraints to plant growth of both fine and coarse textured soils, contributing to their overall fertility. However, it is still uncertain how effective C sequestration practices are for soil physical properties and water retention in practice (Minasny & McBratney 2018).

1.1.2 SOIL PH AND THE CHEMICAL ENVIRONMENT

Soil pH is a measure of soil acidity and alkalinity. It is one of the most important soil parameters, influencing chemical availability of nutrients as well as biological activity (Malik et al. 2018). Most agricultural soils are slightly acidic, with a pH range of 5.5–6.5, while the optimum soil pH for many common crops is around 6.4–6.8 in coarse textured soils, and 6.7–7.0 in fine textured soils. In agricultural soils, the acidic soil conditions are perpetuated by the use of NH_4^+-bearing fertilizers and plant nutrient uptake (Havlin et al. 2016). Plants take up nutrients from the soil in the order $NO_3^-/NH_4^+ > K^+ >> Ca_2^+ > Mg_2^+ > PO_4^{3-} > SO_4^{2-}$ and while doing so, they release either protons (H^+) or hydroxyl ions (OH^-), depending on the type of nutrient taken up (cation or anion). In most cases plants take up more cations than anions, which means that more H^+ is usually released than OH^-. However, the net uptake of ions is highly dependent on the availability of N. As the most important plant nutrient, plants need more N than any other element, and because N can be taken up as either an anion or as a cation, the amount and type of N present in soil often determines the net effect of nutrient uptake on soil pH.

In soil ecosystems, organic N-bearing compounds, such as proteins, amino acids and nucleic acids are mineralized through ammonification. During ammonification, the N in amino groups ($R–NH_2$) is released as ammonia (NH_3) through deamination, which then reacts with water to yield NH_4^+ (**Eq 1**). These process consume H^+ and can counteract the acidificating effect of nutrient uptake or other acidifying processes. However, in cultivated soils much of the plant biomass is harvested and leaving little fresh organic-N to mineralize naturally.

(1) $$R–NH_2 + H_2O \rightarrow R–OH + NH_3$$

$$NH_2–CO–NH_2 + H_2O \rightarrow 2NH_3 + CO_2$$

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^-$$

Under aerobic conditions, NH_4^+-N is rapidly oxidized into NO_3^--N through nitrification, consequently releasing H^+ in the process (**Eq 2**). Nitrification is dominant in agricultural soils and contribute to the acidifying effect of NH_4^+-bearing fertilizers, but is offset by plant nutrient uptake unless NO_3^- is lost through leaching (Havlin et al. 2016).

(2) $$2NH_3 + 3O_2 \rightarrow 2NO_2^- + 2H^+ + 2H_2O$$

$$2NO_2^- + O_2 \rightarrow 2NO_3^-$$

Denitrification is a process where NO_3^--N is progressively reduced to nitrogen gas (N_2) in anaerobic conditions while simultaneously consuming H^+ (**Eq 3**). Furthermore, because nitrification is inhibited in anaerobic conditions, limiting its effect on pH, the pH of frequently water saturated anaerobic soils is often more alkaline than well-drained agricultural soils.

(3) $$2NO_3^- + 4H^+ \rightarrow 2NO_2^- + 2H_2O$$

$$2NO_2^- + 4H^+ \rightarrow 2NO + 2H_2O$$

$$2NO + 2H^+ \rightarrow N_2O + H_2O$$

$$N_2O + 2H^+ \rightarrow N_2 + H_2O$$

Soils have a natural ability to resist acidification as soil constituents bind and release Al^{3+} and H^+. Clay soils owe their buffering capacity to clay minerals, which exhibit permanent negative charge due to isomorphous substitutions while also exhibiting a number of hydroxyl groups (R–OH) at the edges of their mineral sheets (**Fig 4**). Organic-rich soils on the other hand, have a large number of hydroxylic and carboxylic groups (R–COOH) associated with SOM (**Fig 4**). In agricultural soils, these functional groups exist predominately in their dissociated forms ($R–O^-$ and $R–COO^-$) and contribute to soil CEC. As a result, soil properties such as SSA, CEC, and pH buffering capacity are interconnected with the quality and quality of clay minerals and organic matter.

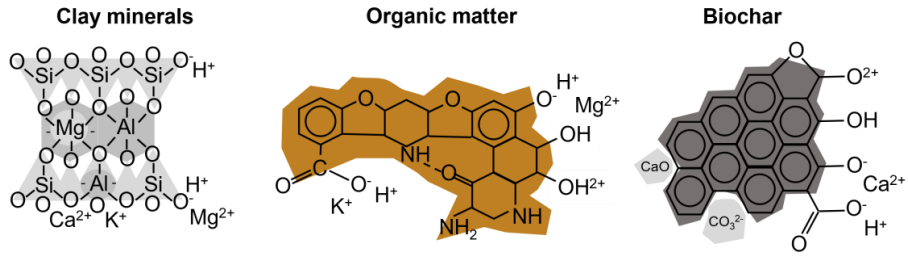

Figure 4 Conceptual representation of clay minerals, organic matter, and biochar showing how they contribute to soil cation exchange capacity through isomorphic substitution or to pH buffering through functional groups, such as hydroxyl ($R–O^- + H^+$) and carboxylic groups ($R–COO^- + H^+$).

In agricultural soils, acidity is managed through liming. This process involves applying acid-neutralizing compounds to soil, especially calcium carbonate ($CaCO_3$), which is often used as the standard for evaluating the liming potential of other materials. Along with neutralizing acidity, liming materials often contain base-cations like Ca^{2+} and Mg^{2+}, which replace a portion of the H^+ and aluminum ions (Al^{3+}) at the cation exchange sites. This helps to address acidification caused by loss of base-cations. Additionally, adding base-cations can have a positive impact on soil structure, as polyvalent cations are capable of binding soil particles together and forming cation bridges between them (Soinne et al. 2014, Heikkinen et al. 2019).

The impact of soil pH and cation balance is typically viewed through the lens of plant production, but it also has a significant influence on soil microbial diversity, richness, and activity, as well as the ratio of bacteria to fungi (Wardle 1998, Fierer & Jackson 2006). Neutral soils tend to have the highest bacterial diversity, while strongly acidic soils have the lowest. In acidic soils, fungi are likely to dominate due to their wider pH tolerance compared to bacteria. Nonetheless, it is challenging to study the influence of acidity on soil microorganisms since gradual pH changes from management practices (Kemmitt et al. 2006, Baggs et al. 2010) may yield a different outcome than abrupt changes caused by liming (Baggs et al. 2000, Šimek & Cooper 2002). Together soil conditions and nutrient availability play a crucial role in determining the quantity and quality of GHG emissions from soils.

1.2 GREENHOUSE GAS EMISSIONS FROM AGRICULTURAL SOILS

After the beginning of the Industrial Era (since 1750), the atmosphere's levels of CO_2, CH_4, and N_2O have been increasing due to human activities such as fossil fuel consumption and land use changes. These three GHGs altogether contribute to approximately 80% of the total radiative forcing caused by GHGs, making them the primary driving forces behind climate change (Shakoor et al. 2020).

Therefore, it is essential to monitor and regulate anthropogenic emissions of CO_2, CH_4, and N_2O to address climate change.

Although soils are ultimately a source of GHG emissions, they can periodically act as either sources or sinks for atmospheric CO_2, CH_4, and N_2O. Agricultural soils account for approximately 10–14% of the annual global anthropogenic GHG emissions (IPCC 2013, Tubiello et al. 2015), largely resulting from the intensive cultivation practices that followed the Green Revolution (since 1960). Climate-smart agriculture aims to mitigate agricultural soil degradation, climate change, and improve agricultural production potential as well as resilience to climate change by promoting practices that optimize the C and N cycles in the agricultural systems (Smith 2012, Paustian et al. 2016). These practices include restoration of degraded land, restoration of wetlands, crop rotation, cover crops, organic fertilizers, liming, organic soil amendments, and minimum tillage (Paustian et al. 2016). However, large scale adaptation of these practices in various climates and into various types of soil, could unintentionally increase GHG emission, which could offset the positive impact of climate-smart practices on climate change mitigation (Smith 2012, Powlson et al. 2011b). Therefore, it is crucial to investigate climate smart practices that introduce C and nutrients into the soil system and how they impact soil processes that contribute to GHG emissions.

1.2.1 SOIL CARBON DIOXIDE EMISSIONS AND CARBON SEQUESTRATION

Natural soils lose from 30 to 75% of their SOM when they are adopted for cultivation (Paustian et al. 199, Stavi & Lal 2013). This has led to a global loss of 40–90 Pg C over the past 150 years (Schimel 1995, Lal 1999, Houghton 2008). This trend is expected to continue due to conventional farming practices and a warming climate (Lal 1999, Houghton 2008, Allison et al. 2010, Heikkinen et al. 2013, Steinmann 2016). The loss of SOM negatively impacts soil fertility, but this issue is often overlooked in industrialized agriculture, which rely heavily on external inputs such as chemical fertilizers, pesticides, fossil fuel, and intensive soil management (Tillman 1999). To reverse the loss of SOM, less intensive management systems like grasslands could be adopted, as they tend to have larger C stocks due to greater C inputs and lower C outputs (Guo & Gifford 2002). Similarly, turning unfertile soils into forestland could restore their C stocks, transforming them from sources of CO_2 into sinks of CO_2. However, sustainable agriculture requires that we also increase soil C stocks alongside crop production.

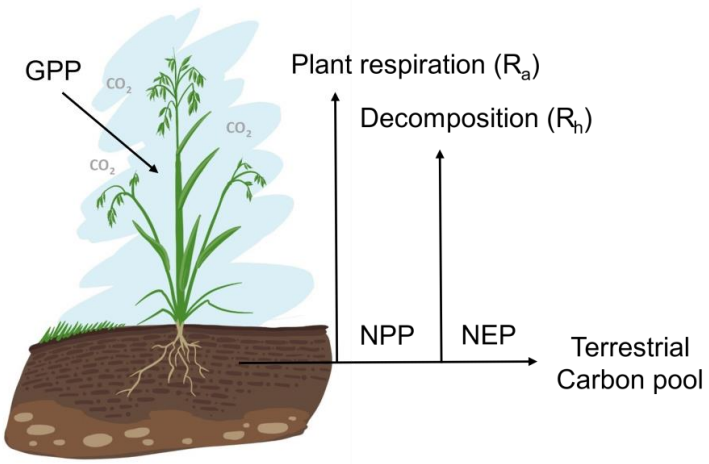

Figure 5 Global terrestrial carbon uptake. Plants fix CO_2 from atmosphere into plant biomass (GPP=Gross Primary Production). Approximately 50% of the C taken up by plants is released back to the atmosphere through (autotrophic) respiration (NPP=Net Primary Production). The uptake of CO_2 is mostly balanced out by decomposition (heterotrophic respiration) of litter and soil organic matter (NEP=Net Ecosystem Production) (adapted from IGBP 1998).

Carbon sequestration into agricultural soils refers to the process of capturing CO_2 from the atmosphere and storing it in the soil as OC. This is achieved through photosynthesis, where plants take up CO_2 from the atmosphere and convert it using solar energy into organic matter and O_2 (GPP=Gross Primary Production). Approximately 50% of the C taken up by plants is annually released back into the atmosphere through autotrophic respiration (R_a, Lloyd & Farquhar 1996, Waring et al. 1998, **Fig 5**) while the rest is retained in various forms of OC (NPP=Net Primary Production) and can remain in the ecosystem for long periods of time. This sink of atmospheric CO_2 is balanced out by decomposers, which release approximately equal amount of C back into the atmosphere through heterotrophic respiration (R_h). This means that the annual net exchange of C between terrestrial sinks and sources is close to zero (NEP=Net Ecosystem Production). Therefore, to increase soil C stocks, we need to either raise C inputs into terrestrial C pools or to reduce C outputs from them.

There are several ways to increase C inputs into soils, such as improving soil fertility, which typically leads to higher GPP. This results in fresh biomass that supports active C and N cycling, and soils with higher SOM typically have higher productivity, decomposition, and mineralization rates, as well as higher microbial biomass and diversity (Prommer et al. 2020). However, increasing C inputs can lead to positive priming (Kuzyakov 2010), in which the fresh C stimulates the decomposition of native SOM (Keiluweit et al. 2015). Therefore, increasing the amount of plant residues incorporated into soil have rarely a noticeable effect on SOM content in intensively managed agricultural soils where the pool of actively cycling C is maintained by constant very large inputs of C (Leifeld & Fuhrer 2010). This is also true for other properties affecting soil fertility, such as soil pH (Kemmitt et al. 2006). In contrast, the goal of C sequestration is to provide long-

lasting and persisting changes that increase SOM and benefit soil fertility (Paustian et al. 1997, Mao et al. 2012, Stockmann et al. 2013). Therefore, C sequestration often relies on means that reduce C outputs without impairing important soil properties like microbial activity.

Currently one the most promising long-term solution for C sequestration is to increase the amount of recalcitrant C introduced into the soil (Lehmann 2007), which increases soil OC content and reduces the proportion of the total C that is rapidly cycled back into the atmosphere. This is mostly achieved through the application of external C inputs, like biochar or other organic soil amendments, which contain significant amount of recalcitrant C, such as lignin (Heikkinen et al. 2021). Increasing the amount of recalcitrant C into soils can therefore impact the terrestrial C cycle by reducing the amount of C that is returned to atmosphere while also improving soil fertility through increased soil C stocks. Using organic soil amendments can thus play an important role in mitigating climate change and promoting sustainable agriculture.

1.2.2 NITROUS OXIDE EMISSIONS FROM SOILS

N_2O contributes up to 8% to global warming over a 100 year time period, owing to its relatively long residence time and high global warming potential (IPCC 2013). Additionally, it is currently the most significant ozone-depleting compound emitted to the atmosphere (Ravishankara et al. 2009). Arable soils are the most important anthropogenic source of N_2O emissions and between 60 to 70% of global N_2O emissions originate from microbial driven soil processes (Baggs 2011, Thomson et al. 2012, Tian et al. 2020), including nitrification and denitrification, together with N fertilization and manure management (Syakila & Kroeze 2011, Smith 2017, Shakoor et al. 2020) as well as biological N-fixation. As a result, reducing N_2O emissions represents substantial mitigation opportunities, which can also ameliorate other environmental problems such as eutrophication and NO_3^- pollution of ground and surface waters (Paustian et al. 2016).

Nitrification

During nitrification chemoautotrophic microorganisms oxidize NH_4^+-N (originating from fertilizers and decaying plant and animal matter) into NO_3^--N. This happens in two steps. First, NH_3 is converted by ammonia oxidizing bacteria and archaea such as *Nitrosomonas*, *Nitrosolobus*, *Nitrosovibrio*, *Nitrosopira* and *Nitrosococcus* to nitrite (NO_2^-). This first step is considered the main source of N_2O from nitrification. During the second step, NO_2^- is further oxidized to NO_3^- by ammonia oxidizing bacteria such as *Nitrososphaera* (Schleper & Nicol 2010, Kozlowski et al. 2016). The rate of nitrification depend on soil pH and the availability of NH_4^+-N and O_2. However, since moisture controls diffusion of NH_4^+ and O_2 in soil, N_2O emissions are also highly dependent on soil moisture. Consequently, most nitrification-derived N_2O emissions occur at soil water-filled pore space (WFPS) below 50–60% (Linn & Doran 1984, Shelton et al. 2000, Bateman & Baggs 2005, Thangarajan et al. 2013).

Nitrifier denitrification

In most soil conditions, NO_2^- does not accumulate in soil because it is rapidly oxidized to NO_3^-. However, under low O_2 conditions, specialized nitrifying bacteria may utilize NO_2^- instead of O_2 producing NO, N_2O and N_2, similarly to denitrification (Casciotti & Ward 2001, Wrage et al. 2001). Usually, denitrifying nitrifiers contribute little to the overall N_2O emissions. However, in comparatively dry soils or after rewetting, it has been suggested that nitrifier denitrification can be a major source of N_2O (Davidson 1992).

Denitrification

Denitrification is a process where heterotrophic microorganisms use various nitrogen oxide (NO_x) species instead of O_2 as final electron acceptors. This process results in the conversion of NO_3^- into gaseous products, mainly N_2O and N_2 (Butterbach-Bahl et al. 2013), thereby completing the N cycle (**Fig 6**). On a cellular level, denitrification is controlled by O_2, NO_3^- (electron acceptors) and OC (electron donors) (Firestone & Davidson 1989). Denitrification occurs mainly in low O_2 conditions, such as waterlogged soils at 60–90% WFPS (Linn & Doran 1984, Rochette et al. 2008, Thangarajan et al. 2013). However, some studies have suggested that denitrification can occur even at aerobic conditions (20–50% WFPS) in pockets of anaerobic microsites (Bateman & Baggs 2005). Regardless, the optimum soil moisture for N_2O production in mineral soils is usually at 70–80% WFPS depending on soil type (Smith et al. 1998, Davidson et al. 2000). At higher water contents N_2O is converted to N_2 therefore reducing N_2O emissions (Letey et al. 1980, Arah et al. 1991, Lessard et al. 1996).

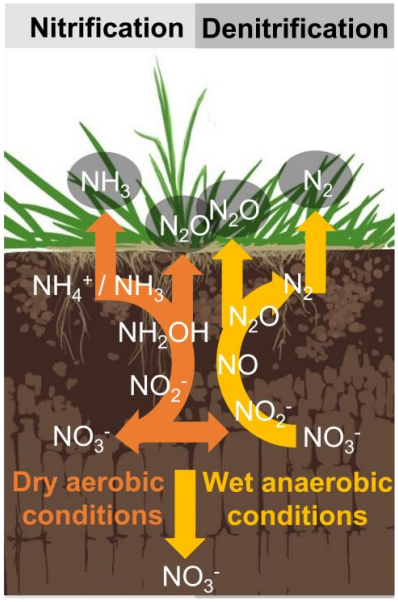

Figure 6 Soil nitrogen (N) cycle consists of various microbial processes that convert nitrogen from one form to another. The cycle can be though to begin with ammonification where organic nitrogen is mineralized to ammonia (NH_3), which exist in soil as ammonium (NH_4^+). In aerobic conditions, NH_4^+-N is rapidly oxidized to nitrate (NO_3^-) through nitrification while in anaerobic conditions NO_3^--N is progressively reduced to nitrous oxide (N_2O) and nitrogen gas (N_2). Nitrogen losses are mainly caused by volatilization of NH_3, N_2O and N_2 as well as NO_3^- leaching.

The taxonomic composition of soil denitrifier communities is very diverse and differ across different soil types, including bacteria, archaea, and fungi. Depending on the dominant microorganisms, the production of N_2O may be affected (Shoun et al. 1992, Laughlin & Stevens 2002, Chen et al. 2014, Maeda et al. 2015). Fungi, for example, are capable of performing both aerobic respiration and denitrification simultaneously, using NO_3^- as an alternative electron acceptor to O_2 (Zhou 2001). However, as many fungi lack the necessary enzyme for converting N_2O into N_2, the end product of fungal denitrification is N_2O instead of N_2 (Shoun et al. 1992). Denitrifier activity is still predominately determined by soil moisture, temperature, pH and the availability of OC. Furthermore, the large functional redundancy means that even if the soil microbial community changes, the overall denitrification activity, and therefore N_2O fluxes, rarely change (Philippot et al. 2008).

Because numerous factors affect production and efflux of N_2O from soils, it is challenging to develop management practices that would reduce N_2O emissions systematically while simultaneously maintaining high soil N contents (Venterea et al. 2012). However, by ensuring that the soil is adequately drained and aerated reduces the chances of anoxic or sub-oxic conditions, which are necessary for N_2O production through denitrification. Increasing SOM content can also be

helpful by improving soil porosity, which in turn, enhances soil aeration and limits denitrification. However, in some cases, increasing denitrification can also be beneficial. For example, improving soil conditions for denitrifiers at the rooting zone can help to reduce the N_2O:N_2 ratio of denitrification (Mørkved et al. 2007, Qu et al. 2014, Cheng et al. 2015, Russenes et al. 2016), and therefore reducing N_2O emissions.

1.2.3 METHANE EXCHANGE OF SOILS

Methane is currently responsible for approximately 20% of global warming due to its high global warming potential for a 100 year time horizon (IPCC 2013, Dalal et al. 2008). Soils play a crucial but somewhat ambiguous role in the global methane CH_4 cycle (Topp & Pattey 1997). Approximately one third of global CH_4 emissions originate from waterlogged soils, i.e., from wetlands and rice cultivation (IPCC 2013), but at the same time well aerated forest soils act as major sinks for atmospheric CH_4 (Le Mer & Roger 2001). Consequently, soils may function as sources or sinks of CH_4 depending on soil conditions and the net effect of methanotrophy (oxidation of CH_4) and methanogenesis (production of CH_4) (Serrano-Silva et al. 2014).

Methanogenesis, the production of methane from soils

Methanogens belonging to the domain archaea are strict anaerobes meaning that they are only active in anerobic conditions. As the least favored redox reaction (Garcia et al. 2000, Dalal et al. 2008), methanogenesis requires that alternative electron acceptors, such as oxygen (O_2), nitrate (NO_3^-), iron ($Fe(OH)_3$), manganese (MnO_2), and sulfate (SO_4^{3-}) have been depleted (Segers & Leffelaar 1996), which is why methanogenesis occurs only after extended periods of anaerobic conditions in waterlogged soils or anoxic microsites (Smith et al. 2003) along with sufficient supply of readily degradable C and at soil pH of 6–8 (Garcia et al. 2000, Yu et al. 2001).

Methanotrophy, the uptake of methane by soils

Methanotrophs consist of aerobic and anaerobic bacterial and archaeal communities that rely on CH_4 as their primary source of C and energy (Smith et al. 2003). These methanotrophic communities are influenced by various environmental factors, including soil moisture, temperature, and pH. Soil moisture plays a crucial role in CH_4 production and consumption, given the low solubility and slow diffusivity of CH_4 and O_2 in water (Grosso et al. 2000). Overall, CH_4 oxidation rates have been shown to dominate in moderately wet soil (<60% WFPS) (Khalil & Baggs 2005), with sharp decline at soil moisture contents below 25% WFPS (Bender & Conrad 1995, Jäckel et al. 2001). Methanotrophic activity occurs over a wide pH range (Saari et al. 2004), with the highest oxidation rates occurring under neutral conditions (Mosier & Delgado 1997). Most natural and agricultural soils act as sinks for CH_4 and subsequently, CH_4 emissions from agricultural soils are often considered negligible (Ball et al. 2004, Thangarajan et al. 2013, Regina et al. 2019), particularly in the case of well-drained mineral soils

(Regina et al. 2007, Dalal et al. 2008). Still, agricultural soils are a net source of GHG emissions and the magnitude of those emissions depend on land use, cultivation practices, and soil conditions (Liebig et al. 2005). As a result, changes in land use and cultivation practices should be evaluated for their impact on GHG exchange.

1.3 ORGANIC SOIL AMENDMENTS AND THEIR USE IN AGRICULTURE

Organic soil amendments are typically nutrient poor byproducts from forest and food industry or bioenergy production and include various composts, digestates, manures, and waste sludges (Ruokavirasto 2023). They are primarily employed for their carbonaceous i.e. carbon rich nature to improve SOM content and associated soil properties. Through soil fertility they have the potential to reduce farming expenses and to improve the premises of crop production. However, their use is presently constrained by the availability of sustainable feedstock, as well as costs associated with technology and transportation (Krotscheck et al. 2000). Furthermore, for farmers to adapt organic soil amendments as part of soil cultivation they need to receive measurable economic and environmental returns that justify the monetary expenses of utilizing such amendments.

To ensure sustainability in the production of soil amendments, it is essential to use renewable and locally sourced materials. **Ligneous**, i.e., wood-derived biomass is the most abundant natural biological material, making it convenient source of soil amendments. In addition, many countries located in the boreal climate zone have extensive forest industries that generate significant amounts of recyclable materials, such as small diameter wood, logging residues, stumps, wood chips, and pulp sludge (Lehmann 2006, Marttinen 2017). Finland and Sweden estimate their annual potential for forest residues to be 40–100 million solid m^3 (Routa et al. 2013). In addition, Finland's forest industry produces 400–600 Gg of pulp sludge per year (Marttinen 2017), while the food industry produces approximately 200–300 Gg of waste biomass, and municipalities generate 600–700 Gg of waste sludge (Marttinen 2017). Much of the waste is disposed by burning and energy production (Gavrilescu 2008), especially in case of forest residues, while others are landfilled (Camberato et al. 2006, Faubert et al. 2016). For example, during 2009, approximately half of the pulp sludge was burned, and in 2012, one tenth was landfilled. However, new legislation has restricted landfilling, and alternative disposal methods, such as soil application, can now be used to recycle carbon and nutrients from the biomass back into agriculture and silviculture. (Camberato et al. 2006, Likon & Trebše 2012, Pervaiz & Sain 2015).

Recalcitrance and decomposition of lignocellulose

Wood fiber is relatively recalcitrant and a rather poor substrate consisting of cellulose (40–45%), hemicellulose (15–35%), and lignin (20–30%), with small quantities of other organic compounds and inorganic minerals. Cellulose itself is

composed of glucose polymers known as cellobiose, which are coupled by hydrogen bonds and van der Waal's forces, creating stacked, sheet-like structures that form a three-dimensional particle. Hemicellulose has a lower degree of polymerization and short side-chains, which distinguishes it from cellulose, and prevents it from forming ordered crystalline structures like cellulose. Lignin, on the other hand, is a phenylpropane-based polymer and the largest non-carbohydrate component of lignocellulose (Sjöström 1993). It consists of three monomers: Coniferyl alcohol, Sinapyl alcohol and *p*-Coumaryl alcohol, each with an aromatic ring and different substituents, forming an amorphous structure with inter-linkages between different lignin monomers and between other polysaccharides. This physical structure contributes to its persistence as it provides steric protection from chemical degradation.

The decomposition of wood residues like branches and small wood occurs relatively slowly (Repo et al. 2011) with a gradual initial colonization phase, followed by a comparatively rapid decomposition of easily degradable C compounds. During this latter phase, soil activity increases and microorganisms produce extracellular substances that bind soil particles together that stabilize soil structure and form soil aggregates (Gagnon et al. 2001, Thies & Grossman 2006). This active decomposition phase lasts for around 10 years, whereas the final slow degradation of lignin can take anywhere from 60 to 100 years (Charest et al. 2004, Mäkinen et al. 2006, Melin et al. 2009, Hubbe et al. 2010, Repo et al. 2011). In contrast, crop residues tend to lose roughly 50% of their mass within the first six months (Stott et al. 1983) and more than 80% within three years (Voroney et al. 1989, Aita et al. 1997).

In cultivated soils the initial colonization of fresh OC by decomposers is influenced by tilling, which incorporates soil amendments into the soil with nutrients and moisture. Still, the degradation of ligneous biomasses follows much the same pattern in cultivated soils as in forest ecosystems. However, during the period of rapid decomposition, lignocellulose decomposition can immobilize soil N due to the high carbon to nitrogen ratio (>30 C:N ratio) of ligneous biomass. Consequently, N mineralization, i.e., ammonification can be expected to be negligible or highly transient in response to application of ligneous biomass (Lehmann & Joseph 2009). In light of this, it is often recommended that soil amendments are applied to soil in autumn, after harvest, when the microbial immobilization of N may actually help to reduce N losses (Wang et al. 2021). Application of carbon-rich biomass may also cause positive priming, i.e., degradation of native SOM (Kuzyakov 2010). However, the net effect is often considered to be C positive, i.e., to provide C sequestration, especially in the case recalcitrant biomasses, such as lignocellulose. Still, the long-term effects, i.e., effects lasting several years after application can be expected to vary depending on the specific characteristics of the biomass, its application rate, as well as the properties of the soil it is applied to.

1.3.1 PRODUCTION AND PROPERTIES OF PULP SLUDGE

Pulp and paper production generates a substantial amount of effluent sludge containing ligneous residues and significant quantities of water used as reaction media or wash water. The waste sludge generated during the process is classified into three primary categories: 1) **primary sludge**, obtained from the primary treatment process, 2) **secondary sludge**, obtained after the wastewater treatment, and 3) **de-inking sludge**, which is produced during paper recycling processes (Thompson et al. 2001, Pokhrel & Viraraghavan 2004, Monte et al. 2009). The average ratio of primary sludge to secondary sludge produced by a pulp and paper mill is approximately 70:30, but this may vary considerably among mills (Meyer & Edwards 2014, Pervaiz & Sain 2015, Faubert et al. 2016). Therefore, the properties of the biomass reflect the quality and composition of the wastewater effluents that are, to some extent, specific to each mill, depending on the type raw material, paper making process, and wastewater treatment (Pervaiz & Sain 2015). However, some properties can be used to characterize each type of pulp sludge (**Table 2**).

Table 2 Average material properties of primary, secondary, mixed, and de-inking pulp sludge (modified from Faubert et al. 2016).

Sludge type	Dry matter (% fresh matter)	Nitrogen (% dry matter)	C:N ratio	pH
Primary sludge	15–57	0.05–0.28	111–943	5.0–11
Secondary sludge	1.0–47	1.1–7.7	8.0–50	6.0–8.5
Mixed sludge	19–60	0.7–3.6	13–31	3.8–8.1
De-inking sludge	32–63	0.15–1.0	34–344	7.2–9.2

Primary sludge

Primary sludge is generated during the primary clarification process, consisting of sedimentation and floatation (Thompson et al. 2001, Pokhrel & Viraraghavan 2004). It is composed of short lignocellulose fibers and mineral fillers that are used in paper production (e.g. kaolin or calcium carbonate) (Pervaiz & Sain 2015). As a result, it has a high C content but low N content, making it unsuitable for use as a fertilizer (Camberato et al. 2006).

Secondary sludge

Secondary sludge, also called biosludge or waste activated sludge, is generated during the wastewater process and is composed of microbial biomass that is produced through the activated sludge process in aerated basins, tanks, or lagoons (Thompson et al. 2001, Pokhrel & Viraraghavan 2004). Most of the fibers and inorganic materials are removed during the primary clarification process. Therefore, secondary sludge has significantly less OC but more nutrients like N and P compared to primary sludge.

Mixed sludge

To regulate the physical and chemical characteristics of the end product, primary and secondary pulp sludge are frequently blended in varying proportions to create mixed pulp sludge (Pervaiz & Sain 2015). Before being discarded, the sludge may also be subjected to procedures such as dewatering, drying, or other treatments.

De-inking sludge

De-inking sludge is created during the process of paper recycling. It is a mix of liquid and solid waste produced during the air flotation process, which is utilized to extract inks and dyes from the recycled paper fibers, as well as from the primary and secondary clarification processes. Consequently, de-inking sludge contains short lignocellulose fibers, adhesives and filler components, color pigments, and de-inking agents, but it is low in nutrients (Simard et al. 1998, Chantigny et al. 1999, Monte et al. 2009).

All of the biomasses mentioned earlier may contain heavy metals, which can cause environmental issues during their disposal (Camberato et al. 2006, Monte et al. 2009, Mäkelä et al. 2012, Pervaiz & Sain 2015). However, the concentrations of harmful substances are usually within the regulatory limits, and pulp sludges can often be used directly as a soil amendments (Camberato et al. 2006). The risk of heavy metal contamination is also reduced by the fact that soil amendments are rarely applied annually like fertilizers.

Before pulp sludge can be applied to soil as a soil amendment it needs to be made biologically inert and a commercially valuable product (Cooperband 2002). This can be achieved through various methods, including lime stabilization, anaerobic digestion, composting, or pyrolysis. These methods can decrease transportation costs, minimize odors, reduce mass and water content, degrade organic compounds detrimental to plant growth, and improve the overall properties of the biomass, thereby increasing its value as a soil amendment (Dick & McCoy 1993, Termorshuizen et al. 2004).

1.3.2 LAND APPLICATION OF PULP SLUDGE

The land application of pulp sludge has been found to have positive effects on soil fertility (N'Dayegamiye et al. 2003, N'Dayegamiye 2006, 2009, Kinnula et al. 2020) and C content (Chantigny et al. 1999, 2000a,b, Fierro et al. 2000). However, the outcome of land application depends on factors such as composition of the sludge as well as frequency and amount applied to soil. Studies have shown that large application rates above 50 Mg ha^{-1} provide longer-lasting effects on soil properties (Vasconcelos & Cabral 1993, Chantigny et al. 2000b, Camberato et al. 2006), while rates below 20 Mg ha^{-1} achieve only short-term effects that persist through the first year (Chantigny et al. 1999, Rasa et al. 2021). Fierro et al. (2000) found that 51% of the applied deinking sludge was decomposed rapidly (half-life 0.4 yr) in a litterbag experiment conducted on a medium-textured sandy mine soil, while the rest was estimated to persist in the long-term (half-life 13 yr). Chantigny et al. (2000b) observed an initial rapid-decay of cellulose-

derived OC during the first 0.1–0.3 yr in two fine-textured soils after the application of 0, 50, or 100 Mg matter ha^{-1} of deinking pulp sludge. This was followed by a much slower degradation of lignin with a mean residence time of 8.5 yr. The two studies suggest that decay of pulp sludge follow the same pattern as wood (Chantigny et al. 2000b) indicating that about 40% of primary, mixed or deinking sludge can be persist in soil after the rapid decay of labile C fractions (Chantigny et al. 1999, 2000a,b, Fierro et al. 2000). However, its influence on soil properties diminishes gradually as more of the lignocellulosic material decomposes (Rasa et al. 2021). Therefore, applications rates equal to or greater than 20 Mg ha^{-1} are recommended to substantially enhance SOM content and other soil properties (Camberato et al. 2006).

The short-term effects of pulp sludge application

Application of easily decomposable OC to soil can bring about significant short-term effects, i.e., changes in soil properties and functionality lasting only one season after application (Nemati et al. 2000). For instance, the high C:N ratio (>30) of pulp sludge can cause significant N immobilization (Chantigny et al. 2013, Faubert et al. 2019), which can limit its appeal as a soil amendment unless additional measures are taken to compensate for N immobilization (Dolar et al. 1972, Aitken et al. 1998, Trépanier et al. 1998, Kinnula et al. 2020). Nevertheless, while N immobilization may hinder plant growth, it can also help to mitigate N_2O emissions resulting from N fertilization (Charles et al. 2017). In a study by Faubert et al. (2017), substitution of chemical N fertilization with pulp sludge, using ratios of pulp sludge to urea ranging from 0:1 to 1:0 of crop N requirements (90–120 kg ha^{-1}), caused asynchrony between crop N uptake and N availability, thereby reducing plant growth (Dolar et al. 1972, Aitken et al. 1998, Simard et al. 1998, Trépanier et al. 1998, Rasa et al. 2021). The study also indicated that pulp sludge application could lower N_2O emissions through N immobilization, especially compared to chemical fertilizers or manure application (Chantigny et al. 2013, Faubert et al 2016, Charles et al. 2017), as long as the supply of N was the limiting factor behind N_2O emissions (Faubert et al. 2016). However, N immobilization is expected to occur only during the first season following incorporation (Chantigny et al. 2013, Faubert et al. 2017, 2019), and therefore its negative effects on plant growth may be overcome with a fallow period (Dolar et al. 1972), or by increasing N fertilization rates (Aitken et al. 1998), or by growing legumes, which rely less on soil N than cereal crops (Allahdadi et al. 2004).

Many soil properties related to microbial activity, such as structural stabilization and aggregate stability, are dependent on the degradation of labile C (Nemati et al. 2000, Janzen 2006). Trépanier et al. (1998) reported the application of deinking sludge at 18 Mg ha^{-1} for 2 consecutive years increased soil structural stability by 20%, but the effect did not persist for more than a year after the last application. Similarly, Nemati et al. (2000) found that a single application of deinking sludge increased wet aggregate stability by 15% and 17% in loamy and silty clay soils, respectively. However, the improved aggregate stability only lasted until the following season after the application, indicating that annual applications were necessary to achieve persistent effects. The authors concluded that microbe-derived compounds, which persist only in the short-term, were

likely responsible for the positive effects on soil stability as the effects did not persist beyond summer months (Nemati et al. 2000, Rasa et al. 2021). Rasa et al. (2021) investigated the effects of a single application of 52, 51, and 72 Mg ha^{-1} of three different pulp sludge materials on soil vulnerability to erosion. They observed that all of the treatments reduced runoff of suspended solids by 30–82% over the four years of consecutive rainfall events in laboratory conditions. Meanwhile, the dissolved OC content of the percolating water was increased by 84–160% in the three pulp sludge treatments, indicating a rapid initial flush of OC (Rasa et al. 2021), which explains why only small portion of the added C was recovered after the experiment.

Incorporating large amount of pulp sludge to the rooting zone can also have positive impact on soil pH. Many pulp sludges contain causticizing substances such as $CaCO_3$ as a byproduct of the pulping and paper finishing processes (Camberato et al. 2006, Nunes et al. 2008). For this reason, pulp sludge could be used as a liming agent, benefitting both plant growth and soil microbial activity (Thangarajan et al. 2013), as well as reducing GHG emissions, particularly N_2O (Šimek & Cooper 2002, Sahrawat 2008, Liu et al. 2010, Bakken et al. 2012, Thangarajan et al. 2013, Faubert et al 2017). For instance, Legendre et al. (2004) found that applying 44 Mg ha^{-1} of primary sludge to a silt loam soil increased the pH of the upper 15 cm soil layer by 0.3 units in one season and 0.8 units after three years. Similarly, Baziramakenga et al. (2001) observed a 0.4 pH unit increase after applying 42 Mg ha^{-1} of composted deinking sludge was applied to the soil.

The long-term effects of land application

Pulp sludge contains recalcitrant components, such as lignin, that can persist in the soil for the long-term and affect soil properties associated with SOM. For example, deinking paper mill sludge has a WHC of 0.36 cm^3 cm^{-3} at -33 kPa and 0.26 cm^3 cm^{-3} at -1500 kPa (Trépanier et al. 1996), exceeding that of most mineral soils. Therefore, mixing pulp sludge with mineral soil should improve soil WHC and create more favorable conditions for plants and soil organisms (Zhang et al. 1993, Chantigny et al. 2000a). However, some studies that have examined the effects of pulp sludge on soil water holding properties have used unrealistically large application rates. Zhang et al. (1993), for instance, reported a 20% and 74% increase at -33 and -1500 kPa respectively with the application of 246 Mg ha^{-1} while Zibilske et al. (2000) observed a 23% point increase in plant-available water (defined as water held between -60 and -1500 kPa pressure) with cumulative addition of 225 Mg ha^{-1} of pulp sludge. Consequently, it is unclear whether the beneficial effects of pulp sludge on soil WHC are simply a result of incorporating a large amount of OC into the soil that is subsequently lost as the carbon decomposes, or whether they are genuinely long-term effects (Baziramakenga et al. 2001).

1.3.3 PRODUCTION AND PROPERTIES OF BIOCHAR

Biochar is a type of charcoal that is produced with the specific intent to improve fertility of forest or agriculture soils (Lehmann & Joseph 2009). A wide range of plant or waste biomass can be used to produce biochar, but wood chips, plant residues, and manure are the most commonly used raw materials, particularly in northern countries. Biochar offers numerous benefits for soil fertility that generally resemble those of SOM, i.e., reduction of BD and increase of soil porosity as well as nutrient and water retention (Cheng et al. 2008). However, biochar is not widely utilized as a soil amendment due to its high cost (e.g. 700–1000€ Mg^{-1}, Salo 2018) and lack of definitive economic returns. Variations in feedstock and charring conditions used to produce biochar, as well as local climate conditions and soil texture, are often cited as reasons for unclear economic and environmental returns. Therefore, investigations that limit these uncertainties should improve the value of biochar as a soil amendment.

Biochar can be produced through various thermal degradation processes, including torrefaction, slow pyrolysis, fast pyrolysis, gasification and combinations of these methods. However, pyrolysis is currently the most widely used process for biochar production because it allows for the simultaneous capture of off-gases emitted during charring, which can be utilized to generate hydrogen, syngas, bio-oils, heat, and electricity (Bridgwater et al. 1999, Demirbas & Arin 2002). As a result, the subsequent sections will concentrate on biochar produced through pyrolysis, while acknowledging that the properties of biochar produced through other methods may differ.

Pyrolysis refers to the degradation of dry or semi-dry biomass at temperatures below 700°C with limited supply of O_2. Wood chips or pellets are commonly used as the feedstock in producing biochar, with a recovery rate of around 50–60% of the OC contained in the original material (Ahmad et al. 2021). Some mass may be regained if volatile compounds are allowed to condense back onto the surface of the biochar, but this should be avoided, as condensates can contribute to the labile C fraction of the final product (Pulido-Novicio et al. 2001) and cause positive priming or N immobilization (Zimmerman et al. 2011, Bruun et al. 2012, Borchard et al. 2014, Singh & Cowie 2014).

The optimal production conditions for land application are yet to be determined. However, moderate temperatures at or below 400–500°C are recommended to produce biochar with relatively high nutrient (N, P, and S) content (Demirbas & Arin 2002, Lua et al. 2004, Lehmann & Joseph 2009). Alternatively, the pyrolysis process can be divided into three parallel pathways based on the temperature and degree of thermal degradation (proposed by Lehmann & Joseph 2009, **Table 3**). These pathways produce biochar with varying carbon contents, including low-carbon biochar (with 40–50% C content), medium-carbon biochar (with 70–80% C content), or high-carbon biochar (with >90% C content).

Table 3 Different classes of biochar produced during pyrolysis at different temperatures (Lehmann & Joseph 2009).

Pyrolysis temperature	Biochar C class	Thermal degradation and end products
<300°C	Low carbon ≤60% biochar	Dehydration and slight degradation of biomass cause release of CO, CO_2 and H_2O vapor.
300 to 600°C	Medium carbon 60 to 80% biochar	More mass is lost, rapid depolymerization of anhydroglucose molecules, which react to form liquid- and tar-products.
>600°C	High carbon >80% biochar	Previously released anhydrosugars degrade further to yield low molecular weight volatile organic compounds, while the strong gasification and carbonization reduce biochar, tar, and liquid formation to a minimum. Large portion of O, H, N, and S is lost through volatilization.

The physical properties of biochar are determined by the feedstock and the temperature used during pyrolysis (**Fig 7**), which control the thermal degradation of the feedstock. At low temperatures, the feedstock loses mainly H_2O and other volatile compounds, followed by the depolymerization, decarboxylation and decarbonylation of cellulose and hemicellulose, leading to the loss of labile C as CO and CO_2 at temperatures ranging from 120 to 250°C. With further thermal degradation, significant mass loss occurs as hemicellulose begins to degrade at temperatures between 200 and 260°C, followed by the more crystalline fractions of cellulose at 240–350°C (Antal & Gronli 2003), Finally, lignin starts to break down between 280 and 500°C (Sjöström 1993). As thermal degradation progresses, the original aliphatic and amorphous structures of the feedstock are replaced by ordered aromatic sheets of the biochar. This process begins at 150°C and continues progressively until 330°C when more aromatic carbon begins to condense. At 350°C, polyaromatic graphene domains start to form, and further degradation leaves only the aromatic carbon matrix behind. Although temperature is often the main factor in biochar production, the feedstock also affects the physical properties of the biochar, particularly at temperatures below 500°C (Laine et al. 1991, Wildman & Derbyshire 1991, Turunen et al. 2020). For example, most biochars have a BD within the range of 0.3 and 0.43 g cm^{-3} and a specific density between 1.5 and 1.7 g cm^{-3} (Byrne & Nagle 1997, Pastor-Villegas et al. 2006). However, biochars made from woody materials have a slightly lower density of 1.47 g cm^{-3} due to their highly porous structure (Oberlin 2002, Brown et al. 2006). The structure of ligneous biochars includes honeycomb-like pores that have a diameter of 10 μm, and these pores act as central pathways to smaller pores (Laine et al. 1991, Wildman & Derbyshire 1991, Rasa et al. 2018). The volatilization of labile carbon during pyrolysis creates new interlinked pores, which enhances the overall porous structure of the biochar and leads to high SSA and WHC (Pietikäinen et al. 2000, Pulido-Novicio et al. 2001, Rasa et al. 2018). Other factors that affect biochar properties include heating rate, pressure, residence

time, flow rate of ancillary inputs, as well as any additional post- or pre-treatments (Antal & Gronli 2003, Lua et al. 2004).

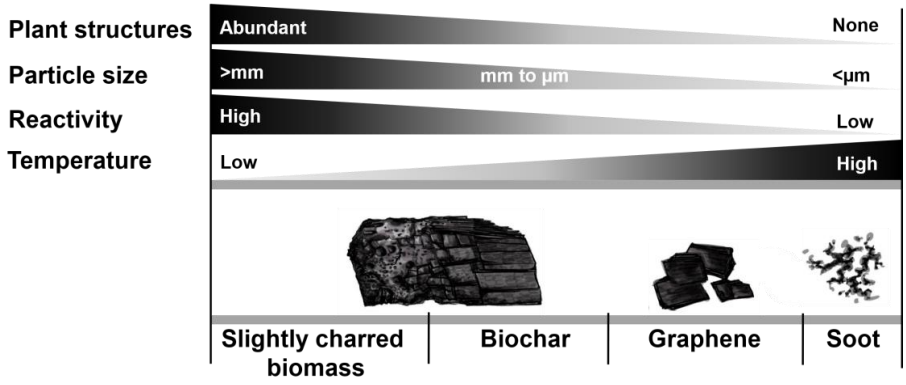

Figure 7 Carbon combustion continuum model predicts that as the production temperature increases the number of recognizable plant structures decreases, as more of the plant material is replaced by polyaromatic graphene domains associated with biochar (modified from Jones & Chaloner 1991, Hedges et al. 2000, Masiello 2004, Hammes et al. 2008).

Biochars are primarily alkaline (with a pH above 7.0), containing high concentrations of CO_3^{2-} and other alkaline compounds such as Ca, Mg, K, Na (oxy)hydroxides, which are often accumulated during the pyrolysis process (Lehmann & Joseph 2009, Soinne et al. 2014, Fidel et al. 2017). However, there is often a limited correlation between pH and liming effect because biochars contain functional groups similar to those in SOM that bind H^+ reversibly (Shi et al. 2017). The quantity and quality of functional groups depend on the thermal degradation (Li et al. 2021, Fan et al. 2022), with carboxylic groups beginning to thermally decompose at 100–400°C, followed by carboxylic anhydrides, and lactones at 427–657°C (Bourke et al 2007). According to Fan et al. (2021), the maximum functionality occurs at 410–450°C. Therefore, although increasing pyrolysis temperature usually increases SSA, it often lowers CEC and the overall surface activity of biochar (Singh et al 2012, **Fig 7**). Therefore, fresh biochar generally has negligible number of functional groups compared to aged biochar because biochar is known to accumulate functional groups while exposed to soil processes (Liang et al. 2006, Cheng et al. 2008, Fan et al. 2018).

1.3.4 LAND APPLICATION OF BIOCHAR

According to current literature (e.g. Tammeorg et al. 2014a,b, Igaz et al. 2018, Borchard et al. 2019, Toková et al. 2020), the recommended approach for applying biochar to increase C sequestration involves applying a significant amount (at least 20 Mg ha^{-1}) to the soil surface and then tilling the soil to a depth of 10 cm, resulting in an application rate of approximately 2% (w/w) (Horák et al. 2021). However, there is no widely agreed-upon optimal application rate for en-

hancing soil fertility (Glaser et al. 2002, Lehmann 2006). Rather, optimal application rates should be considered to differ depending on various factors, such as the biochar's properties, intended use, soil conditions, and the local climate (Lehmann & Joseph 2009).

Effects on soil C stocks, soil structure and soil moisture

Land application of biochar is known to increase soil C content (e.g., Tammeorg et al. 2014a, Nelissen et al. 2015, Blanco-Canqui et al. 2020, Soinne et al. 2020). The increase in soil C content is often attributed to the polyaromatic structure of biochar, which then persists in soil for the long-term. For instance, Soinne et al. (2020) found that 80% of the 30 Mg ha^{-1} of forest residue biochar (produced at 450°C) remained in the top 0–10 cm soil layer a year after its application. Heikkinen et al. (2021) demonstrated that in a 42 day-long microcosm incubation with clay soil as well as with a parallel litter bag experiment, even up to 100% recovery rates are possible with pine biochar pyrolysed at 375°C. On the other hand, Tammeorg et al. (2014b) found that only 18% of the 30 Mg ha^{-1} of debarked spruce (*Picea abies*) biochar (produced at 600°C) remained in the 0–20 cm soil layer 2 years after application. The poor recovery rate was attributed to downward movement of the fine biochar particles, which has been suggested by several authors to impact biochar recovery in coarse-textured soils (e.g., Petter et al. 2012, Tammeorg et al. 2014a,b). This can decrease the effectiveness of fine-textured biochar as a soil amendment in climates with frequent heavy precipitation. Nevertheless, these experiments demonstrate that biochar is highly resistant to degradation and can persist unchanged in the amended soil layer for several years, especially in clay soil, where its translocation by earthworms, root growth, and leaching is expected to be limited.

Biochar has been observed to decrease soil BD (Blanco-Canqui 2017, Razzaghi et al. 2020, Soinne et al. 2020, Toková et al. 2020). Soinne et al. (2020), for instance, reported that biochar decreased the BD of a boreal clay soil, although no improvement in soil porosity was noted. Instead, the changes in BD were ascribed to the mixing of lighter biochar particles with the denser mineral soil (Shepherd et al. 2002, Ulyett et al. 2014). In another study, Tammeorg et al. (2014b) found that a treatment of 30 Mg ha^{-1} biochar reduce soil BD by 6% compared to an application rate of 10 Mg ha^{-1}, which increased soil porosity by 4% in the sampled soil layer (2.5–7.5 cm). However, the differences between the control and biochar treatments were not significant. Furthermore, these effects only lasted for a year, possibly due to leaching of the fine-textured biochar particles. Toková et al. (2020) found a 12% reduction in BD and a 12% increase in porosity of a silty loam soil following repeated application of 20 Mg ha^{-1} of paper sludge and grain husk biochar (produced at 550°C). However, since the study did not examine the effect of biochar application on soil C content, the recovery rate of the added biochar cannot be estimated. Overall, while biochar has been observed to decrease soil BD and increase porosity, it remains unclear if it genuinely promotes the development of soil structure. Hence, more thorough studies on soil structure and porosity are required and should take into account the possibility of translocation by leaching or tillage (Nelissen et al. 2015).

Comprehensive laboratory studies have demonstrated the correlation between biochar pore structure and its ability to hold water (Brewer et al. 2014, Hyväluoma et al. 2018, Rasa et al. 2018, Kameyama et al. 2019, Turunen et al. 2020). Furthermore, many biochar studies have shown that the pore structure of Biochar exhibits significant overlap at ranges with soil pores associated with PAW (Hyväluoma et al. 2018, Kameyama et al. 2019, Turunen et al. 2020). Rasa et al. (2018), for example, demonstrated that biochar produced from willow-derived (*Salix sp.*) and pyrolysed at 320°C had an extensive pore structure similar to fresh wood, with a bimodal maxima at 10 µm and 50 µm. They also observed an increased in WHC at all measured matric potentials, with significant increase above -316 kPa indicating an increase of approximately 17–32% in PAW content (Rasa et al. 2018). Likewise, Turunen et al. (2020) observed that biochar produced from three different feedstock – willow, hemp and mixed wood – also retained their plant tissue-derived pore structure after pyrolysis at 450 to 459°C, with dominant pore diameter of 2–11 µm. Karhu et al. (2011) reported an 11% increase in soil WHC determined using composite samples collected from the top 0–5 cm soil layer, with application rate of 9 Mg ha^{-1}, corresponding to the more commonly used 20 Mg ha^{-1}. Therefore, the addition of biochar to soil should increase its WHC, provided that an adequate amount is added (Ulyett et al. 2014, Igaz et al. 2018, Rasa et al. 2018, Wang et al. 2019, Soinne et al. 2020). However, studies with soils that have a naturally high WHC have rarely shown improvements (Wang et al. 2019, Soinne et al. 2020). In a field study, Soinne et al. (2020) found that soil WHC increased up to a matric potential of -25 kPa with increased proportion of pores smaller than 10 µm and at pore size range of around 25–30 µm, which supports the findings by Rasa et al. (2018). However, the increases in porosity were insufficient to have a significant effect on the soil WHC of the clay soil studied by Soinne et al. (2020).

Effects on NO_3^--leaching and soil N_2O emissions

Studies have demonstrated that the application of biochar can lead to a reduction in soil-borne emissions of N_2O (Cayuela et al. 2013, 2014, Verhoeven et al. 2017, Liu et al. 2018, Borchard et al. 2019), and some long-term investigations have even suggested that this effect can endure in specific types of soils (Hagemann et al. 2017). Denitrification is typically considered the primary source of N_2O emissions from agricultural soils, which is controlled by the supply of labile C, NO_3^--N and O_2 (Butterbach-Bahl et al. 2013), while changes in soil structure, moisture, and aeration can also affect N_2O emissions through their effects on diffusion as well as water and gas flow. Nonetheless, some studies have shown that N_2O emissions and soil NO_3^--N content may be uncoupled (e.g., Kammann et al. 2015, Borchard et al. 2019), indicating that other processes may be involved (Baggs et al. 2010) or that biochar may limit the availability of NO_3^--N. However, there is little evidence that biochar inhibits soil processes related to N_2O emission (Hagemann et al. 2017, Gao & DeLuca 2020), and it is more likely that other factors, such as pH, can explain these observations (Jeffery et al. 2011).

The first meta-analysis on the impacts of biochar on soil N_2O emissions found an average reduction of 54% (Cayuela et al. 2014). However, recent analyses have provided more conservative estimates, ranging from 12% to 38% (Verhoeven et

al. 2017, Liu et al. 2018, Borchard et al. 2019), and there is still little evidence for long-term mitigation (Borchard et al. 2019). Nonetheless, Hagemann et al. (2017) demonstrated with parallel laboratory and field trials that applying powdered beech wood (*Fagus sylvatica L.*) biochar (pyrolysed at 400°C) at a rate of 60 Mg ha^{-1} to a silty loam soil reduced N_2O emissions by up to 68%, even after three years. Kalu et al. (2021b) also found that a single application of softwood (pine and spruce) biochar produced at 550–600°C to sandy clay loam and loamy sand had potential to reduce soil-borne N_2O emissions during periods of high emissions (such as sowing and harvesting) by up to 30% even after eight years. In a related pot experiment Kalu et al. (2021a) found that mixed-wood biochar produced at 400°C also reduced the total cumulative amounts of leached fertilizer NH_4^+-N and NO_3^--N from sandy loam soil by 21 to 54% and 47 to 66%, respectively. The mechanisms behind these observations are still unknown, but several authors have suggested that the likely cause for reduced N losses are sorption and entrapment of NO_3^--N inside the biochar (Kammann et al. 2015, Haider et al. 2016). Saarnio et al. (2018) reported similar findings with spruce biochar produced at 450°C, which systematically retained NO_3^--N and reduced its leaching, in a three-year-long growth experiment conducted with sandy loam soil. They also found that the NO_3^--N content of the topsoil increased with increasing biochar application (0, 10, 20 and 40 Mg ha^{-1}), suggesting a relationship between application rate and reduction in leaching. This supports the idea that the effect is related to physico-chemical properties of the biochar, such as SSA or internal pore structure. In similar fashion, Turunen et al. (2020) proposed that the hydrophobic surfaces of the biochar particles might impede hydrological connectivity between the biochar pores and the soil matrix, which could explain the uncoupling of NO_3^--N and N_2O emissions by affecting the availability of NO_3^--N in combination with soil moisture. In other words, without a continuous water column, the NO_3^--N adsorbed during times of high water content may become trapped inside the biochar pores during drier periods.

Soil pH, as well as liming and buffering of soil pH, have been considered important factors in controlling microbiota in many studies (Bergaust et al. 2010, Jeffery et al. 2011, Cayuela et al. 2013, Obia et al. 2015, Gao & DeLuca 2020). Although many studies have reported small or transient liming effects (Tammeorg et al. 2014b, Hagemann et al. 2017, Soinne et al. 2020), Horák et al. (2021) found that a single application of biochar to moderately acidic soil can effectively increase soil pH for more than four years. This long-term liming effect is attributed to the soluble anions in the ash fraction of the biochar (Noble et al. 1996, Lehmann & Joseph 2009). However carboxylic groups on the biochar surface, particularly in aged biochar, may also contribute to the liming effect (Shi et al. 2017). Due to the uncertainties surrounding the mechanism behind the observed liming effects, it is currently impossible to accurately predict the liming effect of specific biochar products before they are applied to soil.

Effects on CH_4 emissions from mineral soils

The challenges of studying small and variable sources and sinks make it difficult to investigate the exchange of CH_4 between mineral soils and the atmosphere. And even though there is some indication that biochar could potentially

reduce CH_4 emissions from agricultural soils (Karhu et al. 2011, Case et al. 2014), these emissions are often deemed insignificant in the broader context of GHG exchange from mineral soils (Ball et al. 2004, Case et al. 2014, Regina et al. 2007). Therefore, it was decided that CH_4 exchange would not be the focus of this thesis.

2 OBJECTIVES

The objective of this research (**I**, **II**, **III**, and **IV**) was to investigate the impacts of biochar and pulp sludge on soil fertility and GHG exchange in boreal fine-textured mineral soils. This was done by determining their persisting effects on soil C and N cycles, soil structure, and soil pH as well as their subsequent interactions with soil GHG exchange and plant growth. The working hypotheses of the individual studies are listed below.

2.1 STUDY I

H1: Our hypothesis was that, after 2 years the recalcitrant C persisting in soil would not have a long-lasting impact on CO_2 emissions.

H2: Our hypothesis was that the ligneous soil amendments, possessing large SSA and WHC, would improve soil physical properties.

H3: Our hypothesis was that the alkaline nature of the ligneous soil amendments would lead to a notable increase in soil pH.

H4: Our hypothesis was that the physico-chemical changes mentioned previously would have significant impact on non-CO_2 emissions, namely N_2O and CH_4.

2.2 STUDIES II AND III

H5: Our hypothesis was that ligneous soil amendments, weather, and soil cultivation would determine soil CO_2, N_2O, and CH_4 fluxes.

H6: Our hypothesis was that ligneous soil amendments would persist in the soil for the long-term (several years) and improve soil fertility, resulting in improved plant growth.

2.3 STUDY IV

H7: Our hypothesis was biochar retains NO_3^--N through capillary action and hydrophobic interactions.

H8: Our hypothesis was that ligneous soil amendments would persist in the soil for the long-term and improve soil fertility, resulting in improved plant growth.

3 MATERIALS AND METHODS

3.1 EXPERIMENTAL SITES AND EXPERIMENTAL SETUPS

The experimental work (**I**, **II**, **III**, and **IV**) was conducted during 2018 (**I**, **II**, **III**) and 2021 (**IV**). The three field sites were located in different regions of southern Finland (**Fig 7**): **Viikki** in Uusimaa, **Qvidja** in Southwest-Finland, and **Jokioinen** in Kanta-Häme. Approximately 17%, 46%, and 16% of the land area within those geographical regions is cultivated (Lemola et al. 2018), collectively contributing 41% to Finland's overall cropland.

According to national soil surveys conducted in 2005–2009 revelated that approximately 60–70% of fields located in Uusimaa and Southwest-Finland are clay soils whereas in Kanta-Häme, agricultural soils contain less clay soils (~20%), and more coarse-textured soils (>60%) because of glacial ridge formations (Lemola et al. 2018). On average, cultivated soils in Finland exhibited SOM contents ranging from 3.0–5.9% (medium) and 6.0–11.9% (rich). More specifically, in Uusimaa, the proportion of soils belonging to 'medium' SOM class was 30% while 60% belonged to the 'rich' SOM class; in Southwest-Finland, the proportions were 50% and 40%, respectively; and in Kanta-Häme they were both 40% (Lemola et al. 2018). Due to humid climate and soils produced from felsic parent materials, Finnish soils need to be limed regularly to maintain optimum pH (6.0–6.5) (Elonen 1991). According to soil surveys conducted in 1996–2000 most cultivated mineral soils had a pH (H_2O) in the range of 5.5–6.0, indicating that many of them received less than optimal amount of liming (Lemola et al. 2018). Furthermore, because of the young age of Finnish soils (Yli-Halla et al. 2009), many cultivated soils share similar soil properties with the experimental sites, making the results highly relevant for Finnish agriculture.

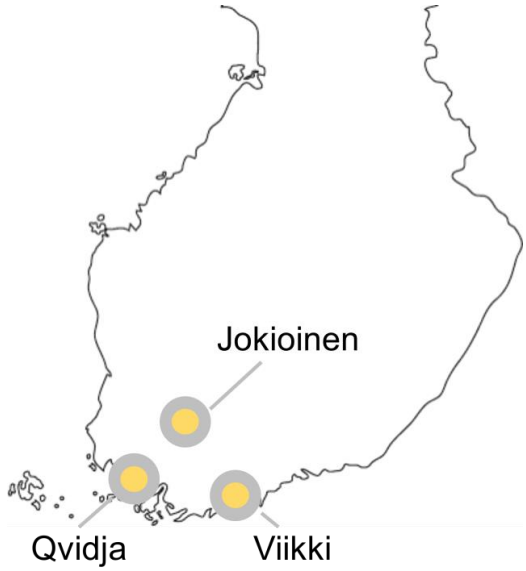

Figure 8 Map of southern Finland with the locations of the three experimental sites: **Qvidja experimental field** located in Parainen, Southwest-Finland; **Jokioinen biochar field** located in Kanta-Häme; and **Viikki biochar fields** located in Helsinki, Uusimaa.

Experimental setup at the Qvidja soil-amendment field

The **Qvidja experimental field** (**I**, **II**, **III**) was established in September 2016 at Qvidja farm (**Fig 8**), in Southwest-Finland (60°17'44.0"N 22°23'35.0"E). The soil has a predominantly clay texture (54%), with 34% silt and 12% sand, and is classified as Cambisol with (Vertic Endogleyic Stagnic) properties (FAO 2006). The average soil C content of 2.4% was the lowest among all the experimental sites but matched the national average. The soil pH before the application of the soil amendments was 6.4 (**Table 4**), which corresponds to fertility class of 'satisfying' (Elonen & Mäntylahti 1996). Prior to 2016, the field had been conventionally tilled with a moldboard to a depth of 20 cm until 2012, and then transitioned to no-till or conservation tillage. The year before the sampling campaign (2017), the field was sown with wheat (*Triticum aestivum*).

The experimental treatments were established using a randomized block design, with three parallel replicate blocks measuring 135 m × 20 m. Each soil amendment treatment was randomly assigned to a 9 m x 20 m plot within each block. The soil amendments were manually applied to the soil surface in 2016 and then incorporated into the top 0.1 m soil layer using Horsch Terrano 3.5 FX cultivator. In 2018, the field was tilled to 0.05 m, and sown with oat (*Avena sativa*, cultivar Matty) in mid-May. From 2016 to 2018, all plots except for the unfertilized control (C0), received N-P-K fertilizer at a rate of 80 kg N ha^{-1} per year. Weeding was done manually in June 2018. As a result of extremely dry weather, the field was irrigated once with approximately 40–50 mm of water over an 18-hour period at the end of June by using 11 rotary sprinklers per replicate block. The crop was harvested using a 1.5 m wide field plot harvester (Wintersteiger, Ried, Austria) in August and the straws were collected, leaving the soil bare.

Initially, the Qvidja soil amendment field was established with twelve different soil amendment treatments and three controls. However, eight of the twelve treatments were discontinued after one year (not shown), and the remaining four treatments (FibreS, LimeS, WilB and SprB) together with two controls (C0 and C80N/C80NU) were investigated in the presented studies **I**, **II** and **III** (**Table 5**). Due to the large number of treatments, the number of replications was low. The application rates used in Qvidja varied significantly and were chosen based on reasonable soil management practices (**Table 5**). With biochar, an application rate of approximately 2% (w/w) was used, which corresponds to an average rate of 20 Mg ha^{-1} (dw) mixed into a 0.1 m soil layer (e.g. Vasconcelos and Cabral 1993, Camberato et al. 2006, Tammeorg et al. 2014a,b).

Experimental setup at the Jokioinen biochar field

The **Jokioinen biochar field** (**III**) was established at the Natural Resources Institute Finland (LUKE) Jokioinen experimental field located in Kanta-Häme (60°48′47″N 23°29′55″E) during autumn 2016 (**Fig 8**). The soil consist of clay (64%), with 21% silt and 15% sand (Soinne et al. 2020). The soil is classified as (Vertic Luvic) Stagnosols (Lilja et al. 2017) with an average soil pH of 5.7 (’passable’, Elonen & Mäntylahti 1996). The average soil C content was highest of the three experimental sites, measuring 4.9% (**Table 4**).

The experiment (**III**) included ten 6 m × 10 m plots arranged into five replicate blocks using a randomized block design. The biochar treatments (**Table 5**) were assigned using a randomized block design and manually applied to the soil surface in October 2016. All plots were then tilled to a depth of approximately 0.1 m using a Kongskilde cultivator. In 2017 and 2018, oat (*Avena sativa*) was planted and fertilized with 90 kg N ha^{-1} and 10 kg P ha^{-1}. For further details, see Soinne et al. (2020).

Experimental setup at the Viikki biochar fields

The two **Viikki biochar fields** (**III**), Viikki-1 and Viikki-2, had been established in 2010 and 2011, respectively. Both experimental fields are located at the University of Helsinki Viikki Experimental Farm (**Fig 8**), in Uusimaa (60°13'25.8"N 25°01'40.2"E and 60°13'42.0"N 25°02'34.0"E). Despite their proximity to each other, the fields exhibit distinct soil textures due to glacial formation (Mokma et al. 2000).

Viikki-1 soil is classified as (Luvic) Stagnosol (FAO 2006), with a sandy clay loam texture (Soil Survey Division Staff 1993) consisting of 24 % clay, 26 % silt, and 50 % sand. The field had a soil pH of 6.6 (’Good’, Elonen & Mäntylahti 1996) and soil C content of 3.4% (**Table 4**).

The original experiments (Tammeorg et al. 2014a,b) had been conducted using a split-plot design with four replicates. For Viikki-1, the main-plot factor was biochar application rate (0, 5, and 10 Mg ha^{-1}) and the sub-plot factor was fertilization rate, corresponding to 30%, 60%, and 100% of the recommended application rates for wheat (150 kg N ha^{-1}), turnip rape (130 kg N ha^{-1}), and faba bean (40 kg N ha^{-1}), respectively. Biochar (**Table 5**) was applied using a sand applicator in May 2010 and then incorporated into the top 0.1 m soil layer with a rotary power harrow. Two days after the biochar application the experimental plots

(2.2 × 10 m) were sown with wheat (*Triticum aestivum*, cultivar Amaretto), turnip rape (*Brassica rapa*, cultivar Apollo), and faba bean (*Vicia faba*, cultivar Kontu). Afterwards, the field was tilled with a disc-harrow to a depth of 0.12 m after each growing season.

Viikki-2 soil was classified as (Endogleyic) Umbrisol (FAO 2006), with a loamy sand texture consisting of 2% clay, 15% silt, and 83% sand (Soil Survey Division Staff 1993. The field had a soil pH of 6.4 ('Good', Elonen & Mäntylahti 1996) and soil C content of 3.2% (**Table 4**). Although considered nutrient-deficient with insufficient amounts of Ca, K, Mg, and S, the field had been cultivated for spring wheat (*Triticum aestivum*) and barley (*Hordeum vulgare*) for the previous 6 years using conventional moldboard ploughing to a depth of 0.25 m and conventional fertilizer application. The main-plot factor at Viikki-2 site had been biochar application rate (0, 5, 10, 20, and 30 Mg ha^{-1}) and the sub-plot factor fertilization type (no fertilizer, meat bone meal or organic fertilizer, and mineral fertilizer). For further details, see Tammeorg et al. (2014a,b).

Table 4 Soil characteristics of the four experimental fields (**I**, **II**, and, **III**), including soil classification (FAO), particle distribution divided into Clay (%), Silt (%) and Sand (%), organic matter (OM) content, total carbon (C%) and nitrogen (N%) content, soil acidity (pH_{H2O}), and electrical conductivity (EC).

Studies	Field site	Soil class	Clay %	Silt %	Sand %	OM	C%	N%	pH	EC (mS cm^{-1})	References
I, **II**, **III**	Qvidja	Cambisol (Clayey)	54	34	12	4.6	2.4	0.3	6.4	1.50	Kulmala et al. (2022)
III	Jokioinen	Stagnosols (Clayey)	64	21	15	9.2	4.9	0.4	5.7	0.10	Soinne et al. (2020)
III	Viikki-1	Stagnosol (Sandy clay soil)	24	26	50	6.9	3.4	2.9	6.6	0.14	Tammeorg et al. (2014a)
III	Viikki-2	Umbrisol (Loamy sand)	2	15	83	6.3	3.2	2.4	6.4	0.08	Tammeorg et al. (2004b)

Experimental setup for the growth experiment

The growth experiment (**IV**) was conducted in the University of Helsinki greenhouses located in Viikki campus. The experiment included two biochars (**Table 5**), which were loaded (pre-incubation at +4°C for 14 days) with NO_3^- using 5 ml KNO_3-solution containing either 20 or 35 µg N g^{-1} together with 10 ml of deionized water. This yielded treatments with fertilization rates corresponding to 80 and 140 kg N ha^{-1}. Quartz sand was chosen as an inert growth medium to study the effects of N availability. The biochar were then mixed with the quartz sand (N=4) at rates of 0 (control), 20 (2%, w/w), and 100 (10%, w/w) Mg ha^{-1} of biochar (**Table 5**). The resulting growth media was administered into randomly arranged plastic pots (640 cm^3) and sown with five pre-germinated (2 days) barley (*Hordeum vulgare*) seeds, 3 cm apart and 1 cm deep. Watering was carried

out using watering plates and the plants were fertilized three times with YaraVita Solatrel (P 192 g L^{-1}, K 62 g L^{-1}, Mg 40 g L^{-1}, Ca 10 g L^{-1}, Mn 10 g L^{-1}, Zn 5 g L^{-1}, Yara, Finland) during the 36-day-long experiment. For further details, see Pitkänen 2022.

The biochar samples (5 g, N=4) used to investigate retention and release of mineral- N in a parallel laboratory experiment (**IV**) were incubated for 93 days at +4°C with 10 ml KNO_3-solution containing 20 µg N g^{-1} biochar.

3.2 SOIL AMENDMENTS AND EXPERIMENTAL TREATMENTS

Most of the investigated soil amendments (**I**, **II**, **III**, **IV**) were derived from ligneous, i.e., wood-derived feedstock (**Table 5**). The seven biochar materials were: forest residue[1] biochar and willow[2] biochar (*Salix sp.*) both produced at 450°C by Raussin metalli Ky (Sippola); mixed spruce-pine[3] biochar (*Picea abies-Pinus sp.*) and spruce[4] (*Picea abies*) biochar produced at 600°C by Preseco Oy (Lempäälä); spruce[5] biochar (*Picea abies*) produced at 450°C by RPK Hiili Oy (Mikkeli); walnut[6] (*Juglans sp.*) shell biochar produced at 800–900°C by Carbo Culture Oy (Helsinki); and spruce[7] (*Picea abies*) chip biochar produced at 600°C by Carbofex Oy (Nokia). Additionally, several of the studies (**I**, **II**) included lime stabilized pulp sludge materials, which were provided by Soilfood Oy (Helsinki). The two pulp sludge treatments were mixed pulp sludge without nutrient supplements[8] and mixed pulp sludge composted with manure[9]. The soil amendments were compared to fertilized (C80N) and un-fertilized (C0) controls as well as to an un-dried (C80NU) control in the incubation experiment (**I**). A detailed list of the ligneous soil amendments and their respective material properties can be found in **Table 5**.

Table 5 Experimental treatments and the material properties of the studied ligneous soil amendments (**I**, **II**, **III**, and **IV**), their application rates in dry weight (Mg ha^{-1} dw) and in relation to soil mass (%, w/w), total C inputs to soil, and N fertilization. Each treatment was given an abbreviation referring to either the field sites they were applied to (Jok=Jokioinen and Vik=Viikki), their feedstock (Fibre=primary pulp sludge, Lime=lime stabilized mixed pulp sludge, Spr=spruce, Wil=willow, Nsh=walnut shell), or whether the material was biochar (B and BC) or pulp sludge (S). The table provides information on their production method, cation exchange capacity (CEC), alkalinity (pH), electrical conductivity (EC) total C% and N% content, and specific surface area (SSA). For more information, see references.

Treatments (studies)	FibreS[8] (**I**)	LimeS[9] (**I**, **III**)	SprB[5] (**I**, **II**, **III**)	WilB[2] (**I**, **II**, **III**)	JokB[1] (**III**)	VikB-1[3] (**III**)	VikB-2[4] (**III**)	NshBC[6] (**IV**)	SprBC[7] (**IV**)
Location (year)	Qvidja (2016)	Qvidja (2016)	Qvidja (2016)	Qvidja (2016)	Jokioinen (2016)	Viikki-1 (2010)	Viikki-2 (2011)	2021	2021
Feedstock	mixed pulp sludge	mixed pulp sludge	spruce chips	willow chips	forest residue	debarked spruce/ pine chips	spruce chips	walnut shell	spruce chips
Production method	lime-stabilized	lime-stabilized	retort slow pyrolysis 450°C	continuous slow pyrolysis 450°C	continuous slow pyrolysis 450°C	continuous slow pyrolysis 500–600°C		flash pyrolysis 800–900°C	continuous slow pyrolysis 600°C
Application rate (Mg ha^{-1} dw)	14	9.0	20	22	30	0.0, 5.0, 10	5.0, 10, 20, 30	-	-
Application rate (%, w/w)	1.2	0.8	1.7	1.9	2.5	-	0.4, 0.8, 1.7, 2.5	2.0, 10	2.0, 10
Dry matter (%)	30	37	94	68	12	-	-	96	40
Carbon input (Mg ha^{-1})	5.5	3.3	19	18	24	4.4, 8.8	4.4, 8.8, 18, 26	-	-
Nitrogen fertilization (kg ha^{-1})	80	80	80	80	85+5.0	30%, 65%, 100%	control, bone meal, mineral	80 and 140	80 and 140
pH (H_2O)	9.2	8.9	8.3	9.8	8.2	10.8	8.1	9.6	8.5
EC (mS cm^{-1})	0.05	0.17	0.09	0.30	0.17	-	-	0.87	0.09
C%	41	37	90	75	80	88	88	73	73
N%	0.04	1.0	0.44	1.7	0.8	0.62	0.35	0.43	0.23
SSA (m^2 g^{-1})	-	-	328	1.3*	-	34.1	265	502	567
References	Rasa et al. (2021)		-		Soinne et al. (2020)	Tammeorg et al. (2014a,b)		Pitkänen (2022)	

*Based on anecdotal evidence, the pyrolysis of WilB was incomplete, which likely explains its lower recalcitrance and significantly smaller SSA compared to other studied biochars

3.3 ANALYSIS METHODS

3.3.1 PRE-TREATMENT OF THE INCUBATION SAMPLES

The bulk soil used in the incubation experiment (**I**) was collected from the Qvidja experimental field by combining three soil samples, one from each block (N=3), using an open-face Edelman clay auger (to a depth of 0.1 m). The soil was then stored at 4°C until the following week when it was sieved (Ø=5 mm) and then carefully spread to air-dry at laboratory conditions (21°C). The sieving was done using larger than typical mesh size to homogenize and break down the soil, but to preserve smaller soil aggregates. The residual water content in the air-dried soil samples was approximately 5% (w/w), determined gravimetrically by drying subsamples overnight at 105˚C.

At the start of the incubation experiment (**I**), 50 g of air-dried soil was used for each of the four (N=4) analytical replicates. The sets of four soil samples were then rewetted to different moisture levels: 20%, 40%, 70% and 100% of WHC, which corresponded to approximately 25%, 50%, 75%, and 110% WFPS, respectively. The soil was then inserted into 0.5 L incubation bottles, along with an undried control (C80NU) that was allowed to dry out naturally from field capacity. After the undried controls had adjusted to one of the four moisture levels, they were kept at their respective moisture levels throughout the incubation period. Afterwards, the moisture levels were adjusted periodically after each gas sampling. During most of the experiment, the incubation bottles were left uncapped, covered in black plastic bags to ensure they remained in darkness, and placed at a temperature of 21±0.4°C and relative air humidity of 24±7.0%.

3.3.2 PRE-TREATMENT OF FIELD SAMPLES

The soil sampling at Qvidja (**II**, **III**) was conducted by taking ten individual soil samples from each experimental plot using soil probes (Ø=2.3 cm), with a sampling depth of 10 cm. The soil samples were then combined to create a composite sample for each plot. Afterward, the fresh soil was passed through a 4 mm (Ø) sieve and stored at +4°C until further analyses.

3.3.3 SOIL pH AND LIMING POTENTIAL OF THE SOIL AMENDMENTS

Soil acidity (pH) and electrical conductivity (EC) were determined (**I**) from the bulk soil using three analytical replicates (N=3). Measurements were done with pH meter Consort C860 (Topac Inc., Cohasset, MA, US) from 1:2.5 (v/v) soil-water suspension (Vuorinen & Mäkitie 1955).

The liming potential of the ligneous soil amendments was estimated (**I**) based on the mass concentrations (g kg^{-1}) of base cations (Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}) after converting them into electrical equivalent amounts as follows:

(4) $$\text{Liming potential} = m_i \sum \frac{m_{Ca}}{2} + \frac{m_{Mg}}{2} + \frac{m_K}{1} + \frac{m_{Na}}{1}$$

3.3.4 SOIL ORGANIC CARBON AND THE RECOVERY RATE OF THE SOIL AMENDMENTS

The total soil C and N contents were determined (**I**, **II**) from air-dried soil that was crushed with pestle and mortar and then analyzed using a varioMAX CN analyzer (Elementar Company, Langenselbold, Germany). As the soil was thought to contain a negligible amount of carbonates (CO_3^{2-}), the total soil C content was assumed to equal soil OC content (i.e. C_{tot}=OC). The C_{tot} content was then used to estimate soil C-stocks (Mg m^{-2}) down to 0.1 m soil depth, according to the following calculation:

$$(5) \qquad C_{stock} = C\, \rho_{bd}\, (1 - g)\, z_h$$

where C is C_{tot} (g kg^{-1}), ρ_{bd} is soil BD (kg m^{-3}), g is proportion of gravel (>2 mm), and z_h is thickness of the soil layer (0.1 m). Hereafter the C-stocks will be expressed in Mg ha^{-1}.

The recovery rates (**I**) of the ligneous soil amendments were determined by subtracting the C_{tot} content of the unamended control (C80N) from the amended treatments. We assumed that all of the surplus OC originated from the ligneous soil amendments (**Table 5**), but since we cannot exclude the potential influence of vegetation on soil C content, we will hereafter refer to the surplus OC as apparent recovery rates.

3.3.5 SOIL MINERAL NITROGEN AND TOTAL NITROGEN

Soil mineral nitrogen (NO_3^--N and NH_4^+-N) was determined (**I**, **III**) using 5 g of soil, extracted with 25 mL 1.0 M KCl, shaken for 30 minutes in an orbital shaker (200 rounds per minute), and then filtered through SartoriusTM Grade 3-HW folded filters (diameter 150 mm). Extracts were stored frozen (-20°C) before being measuring with an automated flow analyzer Lachat QuikChem 8000 (Zellweger Analytics, Milwaukee, Wisconsin, USA).

The amount of mineral-N released by the NO_3^--loaded biochar was investigated (**IV**) by extracting the biochar samples (NshBC and SprBC) three times with 50 ml 2 M KCl-solution. The extracts were then analyzed for their NH_4^+-N and NO_3^--N using GalleryTM Plus Beermaster Discrete Analyzer (Thermo Scientific, USA).

3.3.6 SOIL WATER RETENTION AND BULK DENSITY

Soil water holding capacity (WHC) was determined (**I**, **IV**) gravimetrically by filling a filter paper with soil and saturating it with de-ionized water. The soil was allowed to drain overnight and afterwards, three analytical replicates of 5 g of soil were weighed, then dried at 105°C overnight, and weighed again (Priha & Smolander 1999). Results were calculated as grams of water held by gram of dry soil (%, w/w).

For this synthesis the gravimetric moisture contents were transformed to WFPS using the following equation:

(6) WFPS = (soil water content) × (1 – BD / Particle density)

The soil water retention curves (SWRC) and soil BD were determined (**I**, **II**) from nine undisturbed soil cores (d=73 mm, h=48 mm, V=0.20 L) per treatment. Six soil cores were taken from each amended plot: three from the soil surface (0–0.05 m) and three below the managed soil layer (0.20–0.25 m). The first three were used to investigate treatment effects on soil structure whereas the other three were used to investigate the spatial heterogeneity of the experimental field. In future, the two soil layers will be referred to as the amended top soil layer and the unamended deeper soil layer. Although the amendments may have translocated from the top soil to the subsoil, we assumed that the translocation in the clay soil would be slow and that the treatment effects 2 years after their application would be negligible in the deeper soil layer, which was below the tillage depth (10 cm).

The soil cores were first saturated with water, and then used to determine SWRC by plotting measurements of gravimetric water content (w/w) at matric potentials (ψ) 0.0, -0.3, -6.0, -250 and -1500 kPa (Dane & Hopmans 2002). The pressure range from 0 kPa to -6.0 kPa was determined using the kaolin sandbox method (Eijkelkamp Agrisearch Equipment, the Netherlands) and thereafter to -1500 kPa using pressure plate extractors (Soilmoisture Equipment Corp., Santa Barbara, CA, USA) connected to a compressor (Kaeser Kompressoren, Coburg, Germany) via pressure manifold (Soilmoisture Equipment Corp.). Afterwards, the soil samples were dried at 105°C to determine soil BD.

Plant available water (PAW) was defined as the water holding capacity at a pressure range between -6.0 kPa and -1500 kPa (**Fig 3**). Soil particle density (ρ_s) was estimated using a pedotransfer function (**Eq 7**) developed for Finnish soils by Heinonen (1957) based on clay content (%, x_1) and C_{tot} (%, x_2).

(7) $\rho_s = 2.7 + 0.0007x_1 - 0.0416x_2$

Total soil porosity (φ) was calculated (**Eq 8**) using soil BD (ρ_{bd}) and the density of mineral matter (ρ_s).

(8) $\varphi = 1 - \frac{\rho_{bd}}{\rho_s}$

In this synthesis the total porosity (φ) is presented by dividing it into three pore-size classes (**I**): macropores (>50 µm); mesopores (50–0.2 µm); micropores (<0.2 µm). The largest pore size class was considered to represent structural pores, which are closely linked to BD and compaction (Kutílek 2004, Dexter et al. 2008, Sleutel et al. 2012). The smaller pore size classes represent different textural pores, with mesopores serving as habitats for soil microorganisms (Hassink et al. 1993) while micropores function mainly as adsorptive sites for water, gases, and nutrients. The distribution of soil pore sizes was calculated utilizing the capillary rise equation (**Eq 9**) of Young-Laplace where d is the pore neck diameter (Ø in µm), and ψ is the matric potential in kPa (Schjønning et al. 1999).

(9) $d = \frac{300}{\psi}$

3.3.7 GREENHOUSE GAS SAMPLING AND ANALYSES

During the incubation experiment (**I**), GHG fluxes were measured at intervals of 1, 5, 12, 20 and 33 days after initial adjustment of the soil moisture. Before sampling, each bottle was flushed with ambient air from the laboratory's air-main for 10 seconds, sealed tightly with an airtight rubber cap and a closer, and then over-pressurized with 50 mL of ambient air. Using a syringe-fitted needle, four gas samples (20 mL each) were extracted from each incubation bottle at 1, 5, 9, and 24 hours after closing them, and transferred into 12 mL helium-flushed evacuated gas vials (Exetainer®, Labco Limited, Ceredigion, UK).

During the field experiments (**II**, **III**), GHG fluxes (CO_2, N_2O, and CH_4) were monitored using the closed chamber method. This involved placing an aluminum chamber (60 cm × 60 cm × 75 cm) with an inbuilt fan and a HOBO temperature logger (UA-001-64, Onset, Bourne, MA, United States) on top of a 60 cm × 60 cm collar that had been inserted 10 cm into the soil. After that, a gas sample of 20 ml was extracted using a syringe at intervals of 0, 10, 20, 30, and 40 minutes and injected into a 12 ml evacuated vial (Exetainer®, Labco Limited, Ceredigion, UK). Gas sampling was carried out every two weeks, starting from 5, 8, 10, and 13 days after sowing in Jokioinen, Qvidja, Viikki-1, and Viikki-2, respectively. The final measurements were taken 84, 91, 104, and 105 days after sowing in Jokioinen, Qvidja, Viikki-1, and Viiki-2, respectively.

The soil temperature and moisture were monitored during the flux measurements in Viikki and Jokioinen (**III**) using a Testo 720 thermometer (Testo AG, Lenzkirch, Germany; probe length 7 cm) and TRIME-FM time-domain reflectometer (IMKO, Ettlingen, Germany; probe length 10 cm). In Qvidja (**II**), the soil temperature was monitored using HOBO temperature loggers (UA-001-64, Onset, Bourne, MA, United States), while soil moisture was measured with ML3 ThetaProbe (Delta T Devices).

In all cases (**I**, **II**, **III**), the gas samples were analyzed for CO_2, N_2O, and CH_4 using a gas chromatograph (7890A, Agilent Technologies, California, United States) equipped with a flame ionization detector (FID) and a methanizer for measuring CO_2 and CH_4 concentrations, and an electron capture detector (ECD) for measuring N_2O concentration (Pihlatie et al. 2013). The GHG fluxes were then calculated using linear interpolation as follows:

$$\text{GHG emissions} = \sum \frac{(F_i + F_{i+1})}{2} (t_{i+1} - t_i) \quad (10)$$

where F_i is the gas flux (μg CO_2-eq g^{-1} soil h^{-1}) measured during time interval i, and t_i+1-t_i is the time interval between the measurements in hours. For easier comparison, all fluxes were transformed to CO_2 equivalents (CO_2-eq) according to their global warming potential: 25 in the case of CH_4 and 298 in the case of N_2O (IPCC 2013), respectively.

3.3.8 PLANT SAMPLING

During the Qvidja field experiment (**II**, **III**), plant height was measured weekly from five individual oat plants per plot using a ruler. Treatment effects on above- and below-ground plant biomass were assessed using three above-ground samples and five below-ground root samples per plot. The above-ground biomass was cut (Ø=0.20, m=0.0314 m^2) at a height of 0.02 m, whereas under-ground root samples were collected using a soil auger (Ø=0.05 m) to a depth of 0.20 m. Among the five root samples, three were collected from the top of the plant rows and two from the middle of the rows. The above-ground biomass was frozen (-18°C) for 2–3 months before being separated into oat seeds, oat above-ground biomass (stems and leaves), and other biomass (weeds). These samples were then dried for 48 hours at 60°C and weighed to determine their dry mass. The root samples were stored in a refrigerator (+6°C) for 3–7 days before being soaked in water for approximately 30 minutes, after which the roots were manually separated from bulk soil. The root biomass was then dried for 48 hours at 60°C and weighed, after which they were incinerated to determine loss on ignition (2 hours at 550°C).

During the Viikki growth experiment (**IV**), plant growth was monitored three times a week from three individual barley plants per pot. At the end of the experiment, all shoots were cut and roots were washed. Both roots and shoots were then dried at 40°C and analyzed for their C and N content using a 828CN analyzer, (LECO, Germany).

3.4 OVERVIEW OF THE METHODS

Overview of the analytical (**Table 6**) and statistical (**Table 7**) methods used during the laboratory and field experiments.

Table 6 An overview of the analytical methods used in the characterization of plant and soil properties as well as soil GHG (CO_2, N_2O, and CH_4) fluxes.

Soil properties	Studies	Analysis method	Analyzer
Soil and plant total C and N (C% and N%)	**I**, **II**, **III**	Dry combustion method using 0.8 g of powdered air-dry soil, or oven dried (40°C) powdered plant material.	varioMAX CN analyzer, Elementar Company, Langenselbold, Germany; Leco CN828 CN analyzer, LECO Corporation, United States
Mineral nitrogen (NO_3^--N and NH_4^+-N)	**I**, **III**	Single 1.0 M KCl extraction using 5.0 g of sieved soil.	Lachat QuikChem 8000, Zellweger Analytics, Milwaukee, Wisconsin, United States
	IV	Three consecutive 2.0 KCl extractions using 5.0 g of biochar.	GalleryTM Plus Beermaster Discrete Analyzer, Thermo Scientific, USA
Microbial biomass C and N (MBC and MBN)	**I**, **III**	Chloroform fumigation extraction using 8.0 g of fresh soil extracted with 0.05 M K_2SO_4 solution.	Shimadzu TOC–V cph/cpn analyzer, Kyoto, Japan
Soil acidity (pH)	**I**, **II**, **III**	Measured using potentiometric pH meter (1:2.5 H_2O and 0.01 M $CaCl_2$ soil suspension).	Consort C860, Topac Inc., Cohasset, MA, US
Soil water holding capacity (WHC)	**I**	Determined gravimetrically from saturated (DI-water) soil drained overnight.	-
Soil bulk density (BD) Soil water retention curve (SWRC)	**I**, **II**	Under- and overpressure methods using undisturbed soil cores (d=73 mm, h=48 mm, V=0.20 L).	Kaolin sandbox, Eijkelkamp Agrisearch Equipment, the Netherlands Pressure plate extractors, Soilmoisture Equipment Corp., Santa Barbara, CA, USA
Soil temperature and moisture	**II**, **III**	Measured manually using thermometer or remote monitored using automatic data loggers.	Testo 720 thermometer, Testo AG, Lenzkirch, Germany TRIME-FM time-domain reflectometer, IMKO, Ettlingen, Germany HOBO temperature loggers, UA-001-64, Onset, Bourne, MA, United States ML3 ThetaProbe, Delta T Devices
Greenhouse gases (CO_2, N_2O, CH_4)	**I**, **II**, **III**	Syringe sampling (**I**, **II**) using closed chamber technique (**II**, **III**), and gas chromatography; or with Gasmet analyzer (**III**).	Gasmet Fourier transform infrared trace gas analyzer DX4015 HOBO temperature logger; 7890A, Agilent Technologies, Santa Clara, CA, USA

Table 7 An overview of the statistical analyses used during the research.

Statistical test	Studies	Analysis method
Test for homogeneity of variance	**I**, **II**, **III**, **IV**	Homogeneity of variances was tested using the Levene's test.
Test for normality	**I**, **II**, **III**, **IV**	The assumption of normality (p>0.05) was tested using the Shapiro-Wilk test.
Data transformations	**II**, **III**	Whenever the assumptions were violated, the data was subjected to either Box-Cox transformation or logarithmic transformation in order to meet requirements.
Comparison test	**II**	Independent t-test.
Comparison test	**II**	Two-way analysis of variance (ANOVA).
Comparison test	**III**	Linear mixed-effects model.
Comparison test	**I**, **III**	Tukey's post hoc test.
Correlation test	**I**, **III**	Pearson's r.

4 RESULTS AND DISCUSSION

4.1 SOIL PHYSICO-CHEMICAL PROPERTIES

4.1.1 SOIL CARBON CONTENT

The use of biochar and other C-rich soil amendments has been shown to increase soil C content. Based on this knowledge, we hypothesized (**H1**) that the application of recalcitrant C, whether it is aromatic or derived from lignin, would increase soil C content in the long-term. This hypothesis was supported by soil analyses conducted during the incubation experiment in 2018 (**I**), where we observed that LimeS, WilB and SprB treatments had increased SOC content (p<0.05) by approximately 0.14, 0.48, and 1.05 percentage (w/w) compared to C80N. Based on the data, we estimated that the apparent recovery rates of the respective soil amendments were 46%, 46% and 61% of the original C inputs applied 2 years earlier. Whereas, the apparent recovery rate of FibreS was only 16%. However, no significant differences in SOC content were found during the parallel field experiments (**II**, **III**), likely due to differences in sampling procedures and the soil heterogeneity at the Qvidja site. In other words, during the incubation experiment (**I**) we used analytical replicates that were taken from one bulk soil sample that consisted of homogenized soil pooled together from the three replicate blocks. This likely reduced the variation between samples.

Table 8 Total C inputs at the Qvidja site in 2016, and the subsequent soil organic carbon (SOC) contents (±standard errors of the mean, N=4) measured in 2018. The apparent recovery rate was determined by assuming that all of the OC, surplus of the control, originated from the ligneous soil amendments. Statistical differences (p<0.05) are shown using lowercase letters. For abbreviation see **Table 5**.

Treatments	C input 2016 (Mg C ha^{-1})	SOC 2018 (%, w/w)	Soil C-stock (Mg C ha^{-1})	Recovery (%)
C80N	-	2.49±0.02^{a}	29.2±0.28^{a}	-
FibreS	5.5	2.57±0.02^{ab}	29.9±0.25^{ab}	15.8±0.05^{a}
LimeS	3.3	2.62±0.01^{b}	30.7±0.05^{b}	45.7±0.04^{b}
WilB	18.0	2.97±0.02^{c}	37.5±0.31^{c}	46.4±0.02^{c}
SprB	19.0	3.54±0.03^{d}	40.8±0.38^{d}	61.2±0.02^{d}

Our results align with previous studies, which have demonstrated that aromatic and lignin-derived C are more likely to persist in soil. For example, Heikkinen et al. (2021) found that approximately 40% and 60% of fiber sludge and pulp sludge remained after a year in a litterbag experiment, which they associated with lignin-derived C. In our study, we found that approximately 40% of LimeS remained in soil, which we associated with lining-derived C based on the

information provided by the producer of the soil amendments, which also corresponds closely to the apparent recovery rate observed 2 years after its application to soil (**Table 8**). This implies that lignin-derived C makes up most of what remains in soil and that the decomposition of pulp sludge is similar to that of other ligneous materials, such as wood. However, the long-term fate of lignin-derived C is unknown, as repeated application of lignin-rich biomass could cause decomposers to adapt and break down recalcitrant compounds more efficiently, reducing their retention time (Heikkinen et al. 2021). Climate change could also hasten the decomposition of recalcitrant C (Karhu et al. 2010). Nevertheless, our findings together with the existing literature suggests that significant portion of the C in ligneous soil amendments persist in boreal agricultural soils after 2 years. Further studies, with longer duration should be conducted to provide more precise estimations of the persistence of amendment-derived C together with C fractionation studies to reliably identify the persisting C fractions.

The apparent recovery rates of biochar were found to be between 46% and 61%, which is lower than what Heikkinen et al. (2021) or Soinne et al. (2020) reported. Heikkinen observed no loss in mass of pyrolysed pinewood within 1 year, and Soinne found that approximately 80% of the applied 30 Mg biochar ha^{-1} remained after 2 years. Despite the apparent differences in recovery rates, most studies confirm that significant amount of the applied biochar remain in the rooting zone, with some of it being decomposed and some being lost due to physical processes, such as mixing and translocation. For instance, Tammeorg et al. (2014b) found that despite its high recalcitrance, only about 18% of the applied biochar remained after 2 years. This was attributed to translocation of the biochar in a coarser soil texture, while Heikkinen et al. (2021) used litterbags to hold the biochar in place during the experiment, which likely contributed to their high recovery rates. In field studies, the seasonal variation in soil volume due to soil management practices (Håkansson 2005) may cause significant variation in recovery rates, which is a common problem when measuring SOC (Wendt & Hauser 2013). Therefore, future studies should account for the possibility of significant translocation when using fine-textured biochar on coarse-textured soils, and sampling should always be conducted based on equal-soil-mass rather than fixed soil depth or soil volume.

4.1.2 SOIL BULK DENSITY, WATER HOLDING CAPACITY, AND POROSITY

Our initial hypothesis (**H2**) was that the soil amendments would reduce soil BD, while also increasing both total porosity and WHC. We found that all of the soil amendments used in Qvidja (**I**, **II**) reduced BD when the amended soil layer (0–5 cm depth) was compared to the unamended soil layer (20–25 cm) (**Fig 9A**). However, the differences were not significant ($p>0.05$) due to high variation. Still, we observed a strong correlation between the differences in BD (ΔBD) and the differences in SOC (ΔC) content (**Fig 9B**).

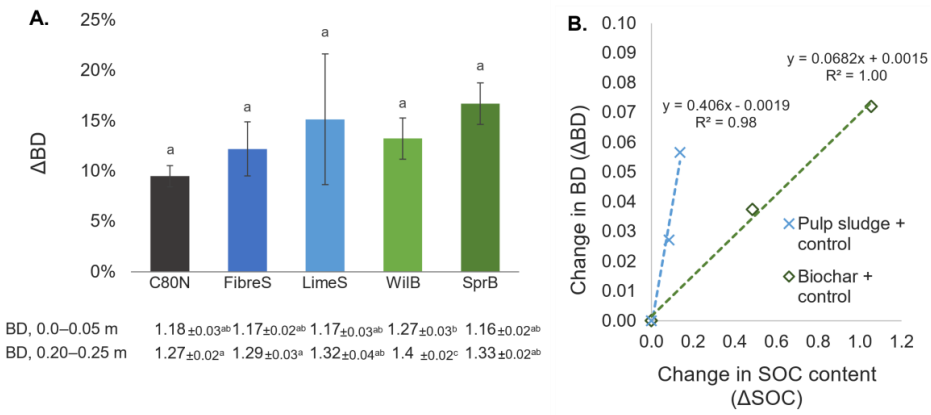

Figure 9 **A**) Mean soil bulk density (BD) measured individually from the amended top soil (0–5 cm) and from the unamended subsoil (20–25 cm). Statistical differences ($p<0.05$) are shown using lowercase letters. **B**) The mean change in soil bulk density (ΔBD) between the top soil layer and corresponding subsoil layer, plotted against the mean change in soil C content (ΔSOC) compared to control (C80N). Both the pulp sludge treatments (FibreS and LimeS) and the biochar treatments (WilB and SprB) include the unamended control as a reference point at origo. The dashed line represent the observed relationship between the persisting amendment C and the change in BD. For abbreviation see **Table 5**.

We found no treatment effects on soil porosity (**Table 9**) except for WilB, which had significantly smaller total porosity compared to C80N (p=0.034, **Table 9**) when the experimental block was used as a covariate. However, after a field scale review of soil physical properties, we discovered that the smaller total porosity and significantly higher BD (**Fig 9A**) in the WilB plots was likely caused by local soil compaction. This compaction was traced back to an open ditch that had previously ran through the experimental field and had been filled with soil. By chance, all of the WilB amended plots were located on the compacted transect.

By using pedotransfer functions, we estimated that the overall soil BD in the experimental field should be approximately 1.2 g cm^{-3}. However, the BD of the compacted experimental plots was 1.3 g cm^{-3}, while the BD of the non-compacted plots was slightly lower than 1.2 g cm^{-3} (**Fig 9A**). The lower values were attributed to tillage, which increases the number of pores between soil aggregates. Furthermore, for soil amendments to improve soil structure they should increase soil aggregation, aggregate stability, or packing of soil constituent. However, aggregation and aggregate stability are often linked to decomposable OC, which means that they are maintained primarily by repeated application of easily decomposable OC (Nemati et al. 2000, Rasa et al. 2021). Therefore, the long-term effects of ligneous soil amendments are likely to be limited to packing density and pore size categories related to internal pores in case of biochar, which exist mostly in the order of 10 µm (Rasa et al. 2018). This was confirmed in our studies (**I**, **II**), where the pulp sludge treatments had no effect on the water retention curve whereas the biochar treatments increased the proportion of pores in the size range of 1.0–50 µm (**Fig 10**).

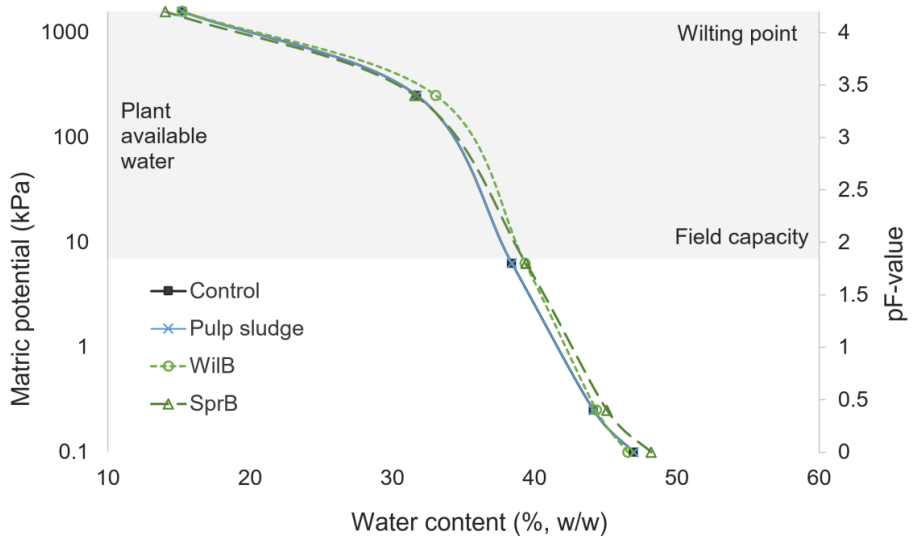

Figure 10 Soil water retention curves (SWRC) determined for the amended top soil layer, including the unamended control plots (Control), mean of all pulp sludge plots (Pulp sludge) as well as willow (WilB) and spruce (SprB) biochar treatments individually.

When considering individual pore size classes (**I**), we found that biochar treatments reduced the proportion of macro- and micropores while increasing (p<0.05) the number of biologically relevant mesopores (**Table 9**). This aligns with the concept of mixing, where biochar particles can be expected to behave much the same way as clay particles and to consolidate themselves to the soil without necessarily increasing the volume of larger pores between soil particles or aggregates. This was most evident in the growth experiment (**IV**) where biochar was mixed with quartz sand. Watering the mixture lead to a tight packing with little air-filled pores. Therefore, it is uncertain whether soil amendments will improve soil structure in fine-textured soils even when BD is reduced. These factors are rarely taken into account when studying the effects of soil amendments, but should be considered important factors in long-term studies.

Table 9 Total porosity and proportion of macropores, mesopores, and micropores. Soil water holding capacity (WHC) and plant available water content (PAW) in the amended top soil. Statistical differences (p<0.05) are shown using lowercase letters. For abbreviation see **Table 5**.

Treatments	Total Porosity (%)	Macropores >50 µm (%)	Mesopores 50–0.2 µm (%)	Micropores <0.2 µm (%)	WHC (%, w/w)	Plant available water (PAW)
C80N	54.7±1.0^{a}	16.7±2.1^{a}	40.2±1.7^{a}	29.0±1.3^{a}	61.0±1.6^{a}	21.7±0.77^{a}
FibreS	54.9±0.9^{a}	14.7±0.9^{a}	40.3±1.2^{ab}	28.2±0.8^{a}	65.5±0.3^{a}	22.1±0.83^{ab}
LimeS	54.7±1.3^{a}	16.6±1.4^{a}	44.0±1.2^{ab}	27.8±0.9^{a}	62.7±1.8^{a}	23.7±0.49^{ab}
WilB	50.8±1.0^{a}	14.0±2.1^{a}	47.9±2.4^{c}	30.1±1.5^{a}	62.2±0.6^{a}	23.2±0.87^{ab}
SprB	54.7±0.8^{a}	16.0±1.6^{a}	46.5±2.0^{ab}	25.7±1.2^{a}	66.3±1.2^{a}	25.2±1.05^{b}

Although the application of ligneous soil amendments had little influence on soil porosity, most of the amended soils exhibited slightly higher WHC. However, the differences were not statistically significant (**Table 9**). This would imply that the potential benefits of ligneous soil amendments are somewhat limited in clay soils. Nevertheless, SprB had significantly larger PAW (p=0.023) than C80N (**Table 9**). Moreover, the differences in PAW between the two soil depths was greatest in WilB, indicating that in conjunction with tilling, biochar treatments may help to mitigate the effects of soil compaction in clay soils. Biochars may also help to alleviate water stress during dry seasons, as evidenced by their larger PAW contents. Nonetheless, the importance of these effects on soil structure and water retention should be verified in future growth experiments.

4.1.3 SOIL pH

Our hypothesis was (**H3**) that all the studied soil amendments would have a liming effect due to their alkaline nature. As expected, all the amended soils sampled in Qvidja (**I**, **II**) had a more alkaline pH than C80N (**Table 10**, p<0.05). The pH of the amended soils was positively correlated (R^2=0.99, p<0.01) with the pH-values (**Fig 11A**) and the application rates of the ligneous soil amendments used in 2016 (**Fig 11B**). The liming effect (ΔpH) observed in this study ranged from 0.4 to 0.8 pH units (**I**), which is consistent with literature (e.g., Soinne et al. 2020, Horák et al. 2021, Kalu et al. 2021). However, there have also been opposing results. Tammeorg et al. (2014a) found that the soil had become more acidic after biochar application (10 Mg ha^{-1}) and only became more alkaline with application rates between 20–30 Mg ha^{-1}. During the following season, soil pH decreased regardless of application rates (Tammeorg et al. 2014a). Additionally, Tammeorg et al. (2014b) did not observe any effects on soil pH at the second Viikki site when biochar was applied at the rate of 5 or 10 Mg ha^{-1}. Similarly, Soinne et al. (2020) found that the liming effect did not have a persisting effects on soil pH in Jokioinen.

Table 10 Soil and amendment pH (H_2O) measured in 2016 as well as in 2018 (H_2O and $CaCl_2$). Amount of Ca^{2+}, Mg^{2+}, K^+, and Na^+ applied in 2016. Statistical differences ($p<0.05$) are shown using lowercase letters. For abbreviation see **Table 5**.

Treatment	pH (H_2O) 2016	pH (H_2O) 2018	pH ($CaCl_2$) 2018	Ca (kg ha^{-1})	Mg (kg ha^{-1})	K (kg ha^{-1})	Na (kg ha^{-1})
C80N	6.4	6.02±0.16^{a}	5.39±0.02^{a}	-	-	-	-
FibreS	9.2	6.77±0.01^{bc}	6.09±0.01^{c}	696	18	3.5	13
LimeS	8.9	6.67±0.01^{bc}	6.03±0.01^{d}	689	8.0	2.8	7.9
WilB	9.8	6.87±0.01^{c}	6.11±0.01^{d}	377	48	211	14
SprB	8.3	6.44±0.00^{b}	5.66±0.02^{b}	217	18	64	1.2

Despite the fact that the two biochar treatments had different physical properties, specifically SSA (**Table 5**), no noticeable differences were observed between their liming effects. Furthermore, no differences in liming effect were observed between biochar and pulp sludge treatments. These findings suggests that the liming effect observed in the studied clay soil was not caused by carboxylic groups or surface oxidation of aged biochar, as has been suggested previously (Shi et al. 2017).

Although biochar ageing may have contribute to soil pH buffering in the long-term, our results (**I**) suggest that the observed liming effect is likely associated with significant increase in base cations. We found that the total liming effect was positively correlated with the total amount of cations, including Ca^{2+}, Mg^{2+}, K^+, and Na^+ (R^2=0.99, **Fig 11A**), as well as with the pH of the biochar and pulp sludge biomasses (R^2=0.91, **Fig 11B**). The relationship between base cations and the liming effect was apparent despite the significant differences in cation composition between pulp sludge and biochar treatments (**Table 10**). While cations do not neutralize acidity, they exist in biochar and pulp sludge together with soluble CO_3^{2-}, silicates, and various (oxy)hydroxides (Lehmann & Joseph 2009, Soinne et al. 2014, Fidel et al. 2017). Furthermore, base cations can also alleviate soil acidification by exchanging H^+ and Al^{3+} ions from soil exchange sites. Therefore, base cations could act as proxies for the total liming effect of pulp sludge and biochar. Moreover, the differences in base saturation and soil CEC could explain the lack of persisting liming effects in Jokioinen compared to Qvidja and the differences in liming effect in Viikki compared to Qvidja. However, we were unable to conduct a more detailed soil analysis regarding CEC and cation composition, and the exact mechanism behind the liming effect remains inconclusive. Despite this, given the various ways in which ligneous soil amendments can affect soil pH and other soil properties, they could be considered a genuine alternative for other liming materials if costs were equal (Shi et al. 2019).

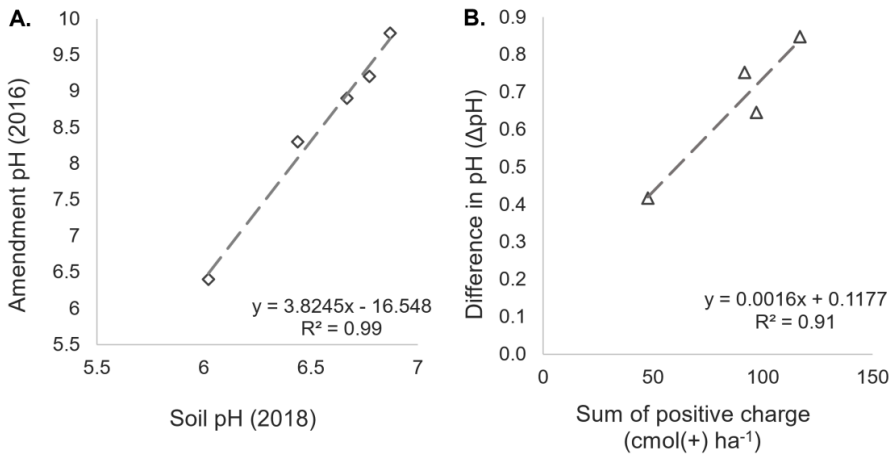

Figure 11 **A**) Correlation between soil pH measured in 2018 and the pH values of the original soil amendment materials in 2016. **B**) The difference in soil pH (treatment pH – control pH = ΔpH) plotted against the total amount of base cations (Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}) applied in 2016 converted into sum of positive charge (cmol(+) ha^{-1}).

4.2 SOIL-ATMOSPHERE EXCHANGE

4.2.1 SOIL GHG EXCHANGE BASED ON LABORATORY EXPERIMENTS

CO_2 emissions from incubated soil

Our hypothesis was (**H4**) that application of ligneous soil amendments would cause significant changes in soil properties and that those would have long-term effects on GHG exchange. We predicted that these effects could be either positive or negative, depending on the interactions between soil moisture and microbial soil processes. In the incubation experiment (**I**), we observed that the estimated total CO_2 emissions increased linearly with increasing soil moisture up to 75% WFPS (**Fig 12**). At a higher moisture level, the rate of increase was slightly reduced, possibly due to reduced diffusion of gases in and out of the water-saturated soil and its impact on soil microbiota. This relationship between soil CO_2 emissions and soil moisture is well-established.

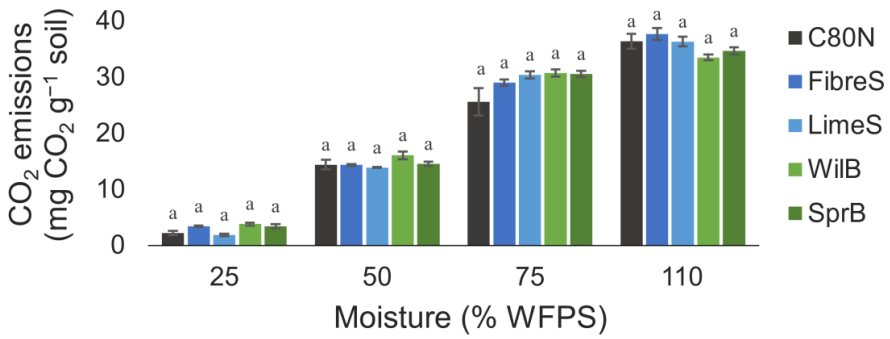

Figure 12 Estimated total CO_2 emissions (mg CO_2 g^{-1} soil) during the 33-day-long incubation experiment (**I**) at four soil moisture levels (25%, 50%, 75%, and 110% WFPS). The error bars represent standard errors of the mean (N=4). Statistical differences ($p<0.05$) are shown using lowercase letters. For abbreviation see **Table 5**.

The CO_2 flux data collected during the incubation experiment (**I**) is presented in **Figure 13** (**A**, **B**, **C**, **D**). From the flux measurements, we can see a clear surge of CO_2 after the soil was rewetted. This response is known as the Birch effect (Jarvis et al. 2007), and it was considered to be part of the treatment effect in the analysis of CO_2 emissions. However, when we excluded the initial surge from the analysis and focused only on the fluxes measured from 5 to 33 days after rewetting, we saw that at 25% WFPS FibreS, WilB, and SprB had higher average CO_2 fluxes than C80N, but equal to C80NU (**Fig 13A**). This is because while C80N had initially higher CO_2 fluxes than the other treatments, the fluxes of FibreS, WilB, and SprB started to increase after 20 days from the initial rewetting. At 50% WFPS, WilB exhibited significantly higher CO_2 fluxes while C80NU had significantly lower fluxes throughout most of the incubation (**Fig 13B**). At 75% WFPS, no differences were observed among any of the treatments after 12 days (**Fig 13C**), whereas at 110% WFPS, all air-dried treatments had slightly higher flux rates (**Fig 13D**).

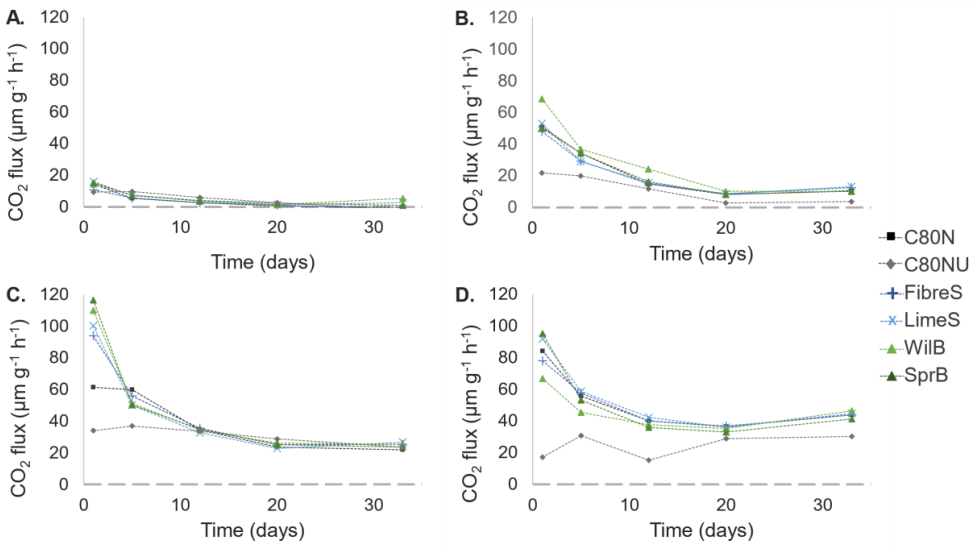

Figure 13 Average soil CO_2 fluxes (µg CO_2 g^{-1} h^{-1}) during the 33-day-long incubation experiment (**I**) at 25% (**A**), 50% (**B**), 75% (**C**), and 110% (**D**) WFPS. For abbreviation see **Table 5**.

After reviewing the incubation data (**I**), we can conclude that the soil amendments had only a limited impact on soil CO_2 emissions. However, at the dry end of the spectrum, there is evidence to suggest that after a prolonged adaptation period, the use of ligneous soil amendments can facilitate microbial activity in dry conditions (**Fig 13A**), which should be considered a positive outcome. Furthermore, it is crucial to consider temporal variation caused by droughts and events of heavy rain, as they can contribute significantly to overall emissions, especially given the increasing frequency of such weather patterns due to climate change.

N_2O emissions from incubated soil

In general, the estimated total amount of N_2O emissions observed during the incubation experiment (**I**) increased exponentially with the soil moisture (**Fig 14**), particularly in the case of C80N. Furthermore, only FibreS, LimeS and WilB treatments exhibited significantly lower N_2O emissions compared to C80N and only at higher moisture contents (**Fig 14**).

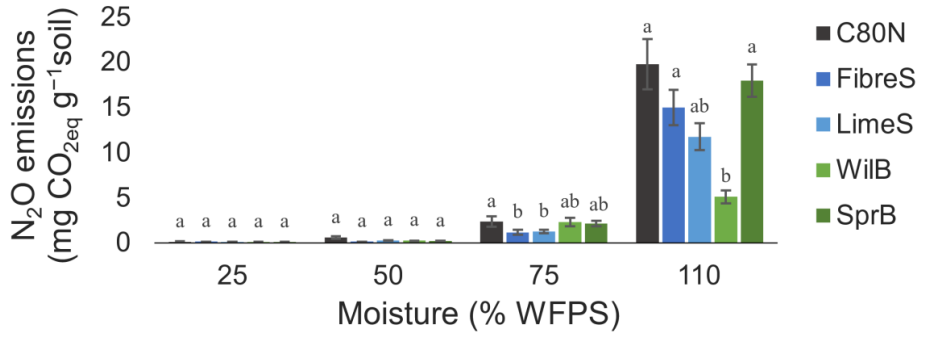

Figure 14 Estimated total N_2O (mg CO_2-eq g^{-1} soil) emissions during the 33-day-long incubation experiment (**I**) at four soil moisture levels (25%, 50%, 75%, and 110% WFPS). The error bars represent standard errors of the mean (N=4). Statistical differences ($p<0.05$) are shown using lowercase letters. For abbreviation see **Table 5**.

The N_2O data (**I**) was re-analyzed and compared to C80NU, similar to the CO_2 data. **Figure 14** (**A**, **B**, **C**, **D**) show that while the Birch effect is often linked to a surge of CO_2 emissions (Jarvis et al. 2007), a similar surge of N_2O emissions is possible when the soil is rewetted. However, the surge is less consistent across the different treatments compared to CO_2 (**Fig 12**). At 25% WFPS only C80N exhibited a clear flush of N_2O, while the other treatments showed the highest flux rates after 5 days of incubation (**Fig 14A**). This suggests that the sampling intervals may have been too long to fully capture the N_2O flux dynamics at the start of the incubation, making total GHG estimations unreliable. Another observation was that in dry soil conditions, the rate of N_2O fluxes begun to increase after 20 days similarly to CO_2 (**Fig 14A**). This could be due to increased nitrification activity resulting from a shift from initial net N-immobilization to net N-mineralization or because of slow adaptation to dry soil conditions since nitrifiers are known to adapt slowly to changes in soil conditions. Nonetheless, the slight increase in N_2O and CO_2 emissions demonstrates the close relations between soil N and C cycles.

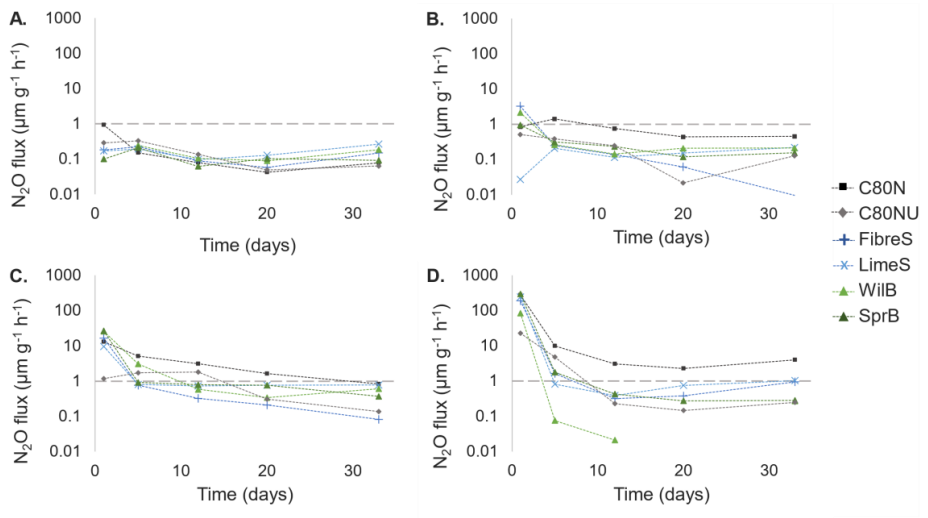

Figure 15 Average soil N_2O fluxes (µg N_2O g^{-1} h^{-1}) during the 33-day-long incubation experiment (**I**) at 25% (**A**), 50% (**B**), 75% (**C**), and 110% (**D**) WFPS. Note that the y-axis in logarithmic scale. For abbreviation see **Table 5**.

In higher soil moisture, N_2O is produced by both nitrification and denitrification. At 50% and 75% WFPS, only the amendment treatments exhibited a surge of N_2O in response to rewetting, while the C80N did not (**Fig 15B**, **C**). Instead, at 50%, 75%, and 110% WFPS, C80N exhibited higher flux rates compared to the amendment treatments (**Fig 15B**, **C**, **D**). Because denitrification-derived N_2O emissions are largely dependent on NO_3^--availability, it is possible that more rapid or more intensive consumption of substrates at the beginning of the experiment could explain the observed differences in the total N_2O emissions (**Fig 14**). The depletion of NO_3^--N was probable, as the soil used in the experiment was collected in autumn when the mineral-N content was low (**Fig 22**). Nonetheless, our findings have significant implications for field and laboratory experiments that rely on periodic measurements of N_2O fluxes to estimate total emissions. In summary, unless the temporal dynamics of N_2O exchange are accurately taken into account, the reported values may be unrepresentative of the treatment effects. We conclude that, based on the presented data (**Fig 14** and **Fig 15**), it is unlikely that any of the amendment treatments reduced gaseous losses of N from the studied soils.

CH_4 emissions from incubated soil

All of the studied soils (**I**) ranged from small sources to moderate sinks of CH_4 (**Fig 16**). However, the relative contribution of CH_4 emissions to the total soil GHG emissions was much lower than that of CO_2 or N_2O emissions, differing by an order of magnitude.

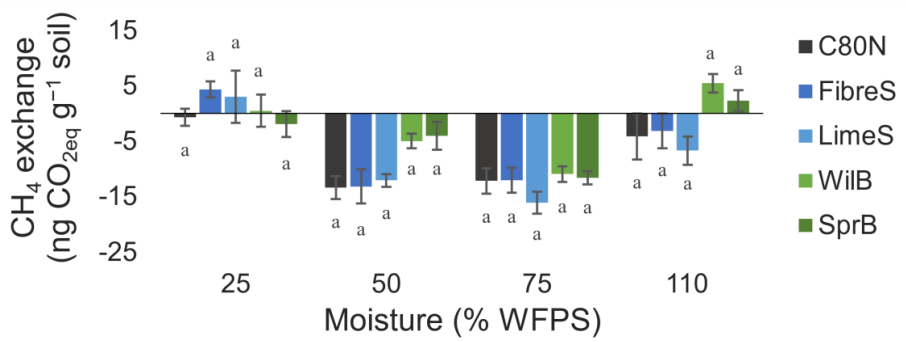

Figure 16 Estimated total CH_4 emissions (ng CO_2-eq g^{-1} soil) during the 33-day-long incubation experiment (**I**) at four soil moisture levels (25%, 50%, 75%, and 110% WFPS). The error bars represent standard errors of the mean (N=4). Statistical differences (p<0.05) are shown using lowercase letters. For abbreviation see **Table 5**.

According to CH_4 flux data, presented in **Figures 17** (**A**, **B**, **C**, **D**), it was observed that all treatments showed similar patterns of CH_4 exchange: initially, CH_4 consumption increased, but after 20 days, CH_4 production started to surpass consumption. This pattern can be attributed to the insufficient buildup of anoxia as well as CO_2, H_2, and acetate in the sieved and air-dried soil. Therefore, it is likely that at the beginning of the experiment methanotrophs dominated over methanogens. As a result, the CH_4 fluxes measured during the incubation experiment may not accurately represent fluxes from cultivated soils. However, many cultivated soils are tilled every spring, which increases aeration and causes the soil to dry out similarly to the air dried soil samples. Therefore, it is unlikely that cultivated mineral soils will become significant sources of CH_4 during the growing season.

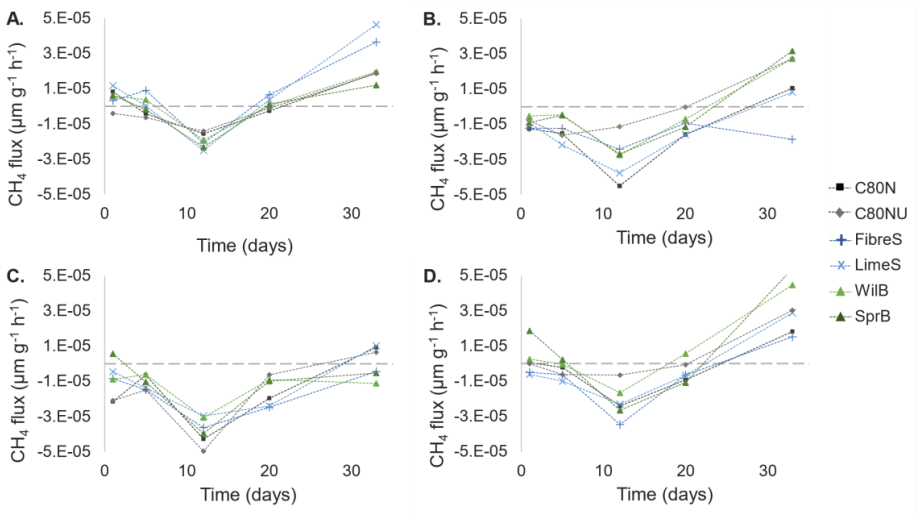

Figure 17 Average soil CH_4 fluxes (µg CH_4 g^{-1} h^{-1}) during the 33-day-long incubation experiment (**I**) at 25% (**A**), 50% (**B**), 75% (**C**), and 110% of WFPS (**D**) For abbreviation see **Table 5**.

4.2.2 SOIL GHG EXCHANGE BASED ON FIELD EXPERIMENTS

Our hypothesis was (**H5**) that ligneous soil amendments would alter soil GHG exchange, both in the laboratory and in the field. Furthermore, we assumed that both weather and soil management would have significant effect on the seasonal variation, and could either amplify or subdue the effects of the ligneous soil amendments.

CO_2 emissions from incubated soil

In general, the amount of CO_2 released from vegetated soil (**II**) was several times higher than from bare soil. This was likely due to autotrophic respiration by plant roots. The highest peak of CO_2 from vegetated plots occurred in July, likely due to increased plant and soil activity after irrigation. Irrigation was necessary because after the snow melted in early April, there was a sudden increase in air temperature in early May, followed by a prolonged period of little or no rainfall until July. On the other hand, CO_2 fluxes from bare soil (**II**) peaked in mid-May (**Fig 18**), immediately after sowing and fertilization. Except for vegetated soil under LimeS and SprB treatments, no apparent effects were found for either vegetated or bare soil treatments (**Fig 18**).

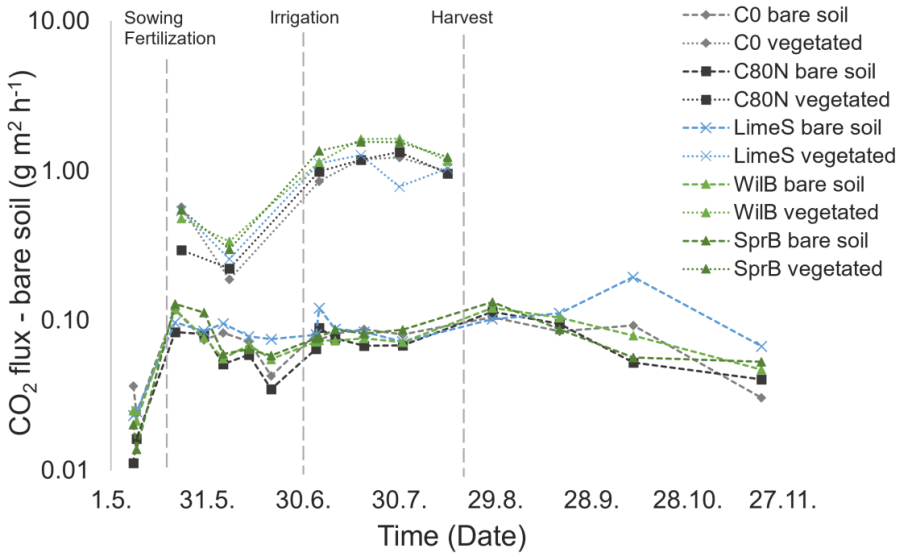

Figure 18 Mean carbon dioxide (CO_2) fluxes from bare soil and from vegetated soil. The field was sown with oat on May 15, it was irrigated on June 30, and the whole field was harvested on August 22. Note that the y-axis is in logarithmic scale. For abbreviation see **Table 5**.

N_2O emissions from incubated soil

Fertilization appeared to have a significant effect on N_2O emissions (**Fig 19**), which was evident from the measured N_2O fluxes, which closely reflected the conversion of soil NH_4^+-N into NO_3^--N at the beginning of the growing season. This suggests that the primary source of N_2O emissions during the early summer was nitrification or coupled nitrification-denitrification (Davidson 1992). This is supported by the observation that the total amount of mineral nitrogen in C80N remained stable between May and June, at around 80.9 to 81.0 mg N kg^{-1} soil (**Fig 20**). However, the proportion of NH_4^+-N in C80N decreased from 61% to 37%, which corresponded with a proportional decrease in N_2O production (**Fig 21**). In addition, N_2O fluxes reached their minimum level in June after the soil was depleted of NH_4^+-N.

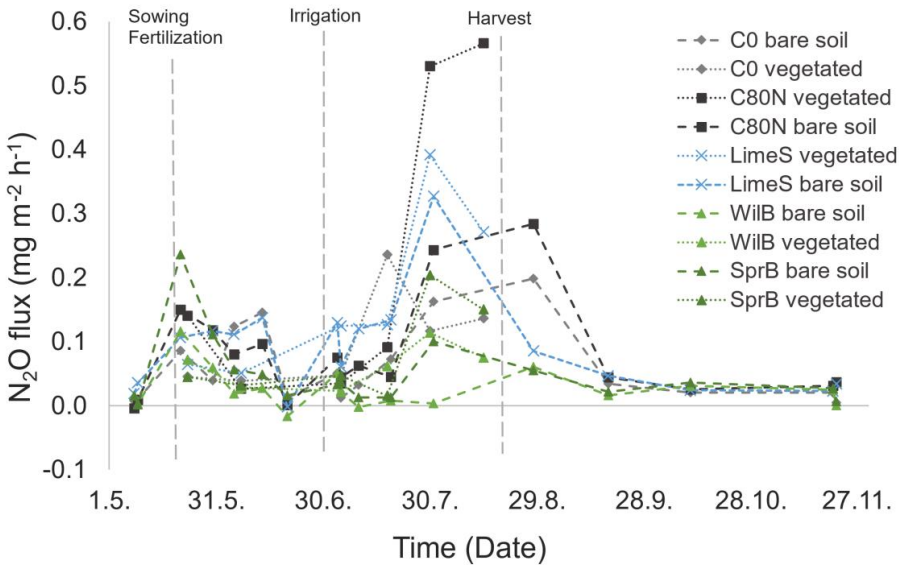

Figure 19 Mean nitrous oxide (N_2O) fluxes from vegetated and from bare soil plots. The field was sown with oat on May 15, it was irrigated on June 30, and the whole field was harvested on August 22. For abbreviation see **Table 5**.

N_2O emissions resumed after precipitation wetted the soil at the end of June, and after that, the N_2O fluxes appeared to follow the soil moisture until the harvest at the end of August (**Fig 19**). In bare soil, C80N and LimeS showed significantly higher N_2O fluxes than WilB, which was consistent with the incubation experiment (**I**), where WilB exhibited the lowest total N_2O emissions at higher water content (**Fig 14**). Furthermore, WilB had the highest NH_4^+-N concentrations (**Fig 20**), which often indicates anaerobic soil conditions (Ponnamperuma 1984). On the other hand, FibreS, LimeS, and SprB had lower mineral-N concentrations in May than in June (**Fig 20**), indicating that additional organic-N may have been released from organic sources. This is particularly true for SprB, which had higher NH_4^+-N concentrations in June than in May, whereas FibreS and LimeS did not (**Fig 20**). N_2O fluxes remained stable after the harvest, exhibiting similar levels that were observed in the incubation experiment (**Fig 14**). Overall, the ligneous soil amendments had little effect on N_2O emissions.

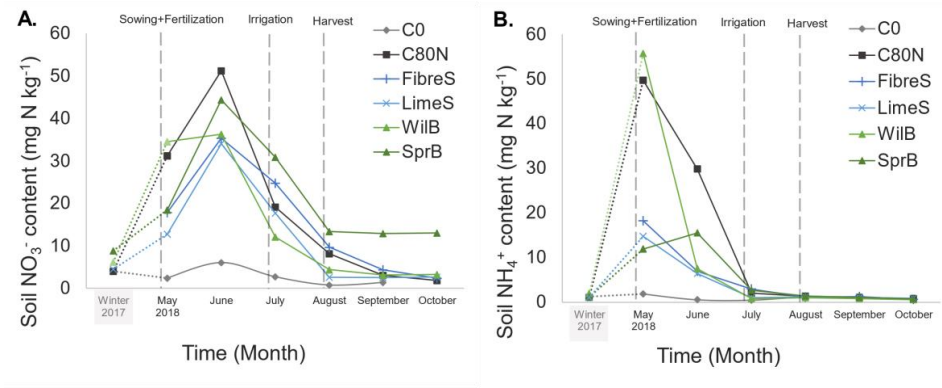

Figure 20 Monthly mean soil **A**) nitrate (NO_3^--N) and **B**) ammonium (NH_4^+-N) concentrations during the 2018 growing season as well as the previous winter. For abbreviation see **Table 5**.

During the field studies (**I**, **II**, **III**), it was observed that SprB was found to retain NO_3^--N while WilB did not. This was most evident in the months of August, September, and October, as SprB had up to six times more NO_3^--N than the other treatments (**Fig 20A**). Moreover, SprB had slightly higher NO_3^--N content during the previous winter in 2017. Despite the significantly higher ($p<0.05$) NO_3^--N concentrations, SprB did not exhibit higher N_2O fluxes in the field study (**Fig 19**) or incubation experiment (**Fig 14**). Therefore, it is possible that in addition to retaining NO_3^--N, SprB also restricted its utilization by microorganisms through other means.

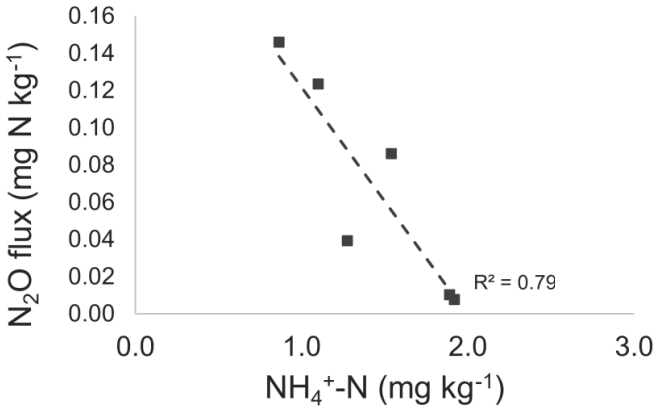

Figure 21 Mean nitrous oxide (N_2O) fluxes from bare soil plots between May to July plotted against soil ammonium (NH_4^+-N) content from the same time period.

CH_4 emissions from incubated soil

For CH_4, all bare soil treatments emitted CH_4 in mid-May after the soil was plowed and fertilized. Later in the season, the CH_4 exchange was close to zero, and no significant differences were observed between treatments (**Fig 22**).

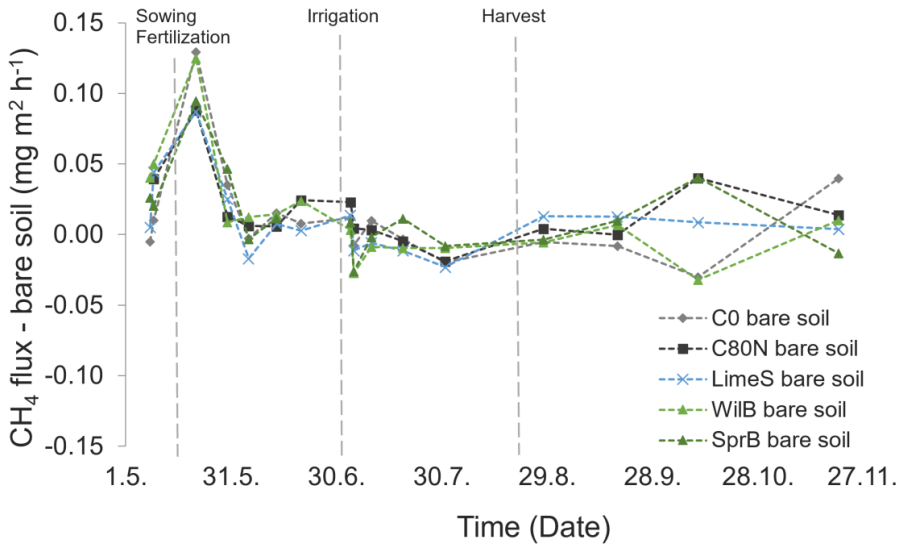

Figure 22 Mean methane (CH_4) fluxes from bare soil plots. The field was sown with oat on May 15, it was irrigated on June 30, and the whole field was harvested on August 22. For abbreviation see **Table 5**.

4.2.3 NITRATE RETENTION BY BIOCHAR

The measurements conducted during the field studies (**I**, **II**, **III**) showed that biochar (SprB treatment only) had the ability to increase and maintain higher levels of soil NO_3^--N than what is naturally found in the soil. We hypothesized that biochar's unique physical parameters, such as high SSA, WHC, and hydrophobicity, contributed to this ability (**H6**).

The only major difference between WilB and SprB was their SSA (**Table 5**). It is possible that the differences were due to unstable pyrolysis conditions, and that WilB had an undeveloped pore structure because of it or that residues blocked its pores. However, Rasa et al. (2021) reported that biochar may also exhibit different pore structures due to differences in feedstock. Nevertheless, differences in volume and architecture of internal pores could explain the differences in NO_3^--N retention through capillary forces, which influence the flow of soil solution and may also have an affinity for anions like NO_3^-. However, it is also possible that the apparent lack of NO_3^--N retention by WilB was related to soil compaction, which limits O_2 diffusion and can cause anaerobic conditions that prevent nitrification and promote denitrification, therefore consuming NO_3^- or preventing its formation. In fact, WilB had the highest soil NH_4^+-N content of all treatments in May (**Fig 22B**), which often indicates anaerobic conditions (Ponnamperuma 1984). Therefore, based on field data, it is unclear which mechanism contributed to NO_3^--retention.

After the field studies (**II**, **III**), a separate study (**IV**) was conducted to further investigate NO_3^--retention in biochar. In that study NO_3^--loaded biochar was extracted in the laboratory, using three consecutive KCl extractions. Another set of

samples was used in a growth experiment to study the effects of NO_3^--retention on plant growth. Since the original biochars used in Qvidja were not available, different biochar materials were chosen from the available commercial biochars. Both biochar materials were found to retain NO_3^--N, but their release dynamics differed significantly (**Fig 23**). The spruce chip biochar (SprBC) released up to 80% of the added NO_3^- during the three consecutive extractions, while the higher temperature walnut shell biochar (NshBC) released less than 2% of the amount of NO_3^- added as KNO_3-solution. In both cases, additional extractions would have likely increased the recovery rate of NO_3^--N as NshBC released mineral-N only after the third and final extraction, whereas SprBC likely contained more NO_3^-N even after three extractions. The retention dynamics corresponded with our expectations, and could be explained by our hypothesis. During preincubation biochar absorbs the KNO_3 solution, into its interpores and because of capillary forces it is retained there even during extraction as at least 0.03 bar of pressure would be required to empty small capillaries present in biochar (10 µm, Rasa et al. 2018). Therefore, the solution inside the capillaries is only diluted by the solution used during the extraction. Release is made more difficult in the high temperature WshBC by its hydrophobicity, which prevents continuous water columns from forming between the extractant and the solution held within the internal capillaries (Turunen et al. 2020). However, we cannot explain the high amount of NH_4^+-N released during the final extraction, and further studies are required to explain all our observations. Regardless, according to our findings, the standard method of extracting soil samples with 2 molar KCl solution significantly underestimates the NO_3^--N levels present in biochar amended soils (Kammann et al. 2015, Haider et al. 2016, Hagemann et al. 2017). Therefore, future studies involving biochar-containing soils should use repeated extractions to determine mineral-N content.

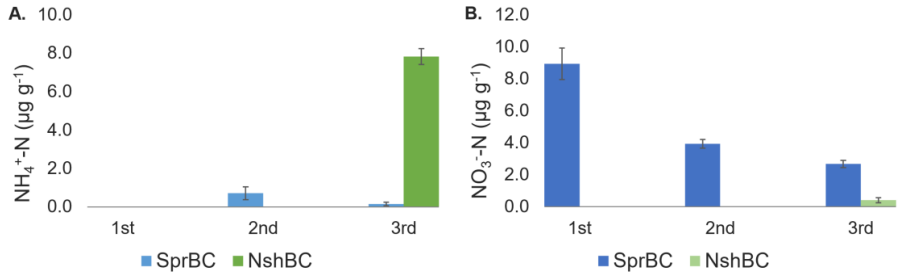

Figure 23 **A**) Ammonium (NH_4^+-N) and **B**) nitrate (NO_3^--N) nitrogen extracted from walnut shell biochar (NshBC) and spruce chip biochar (SprBC) by three consecutive 2 M KCl extractions. Error bars represent standard deviation (N=4).

The available evidence suggests that the retention potential of the studied biochar treatments increased in the order of WilB<SprB<SprBC<NshBC, with the unsuccessfully pyrolysed WilB having the lowest and the high temperature NshBC having the highest. This would indicate that retention was influenced mainly by the production temperature. Consequently, production temperature is known to influence biochar porosity as well as surface properties (Das et al. 2021). This was supported by our observations that biochars produced at higher temperatures (SprBC and NshBC) had larger SSA than those produced at lower temperatures (**Table 5**). Furthermore, the SSA of the high temperature biochar was unaffected by grinding indicating that SSA was mostly determined by their internal pore structure. As production temperature also increases the hydrophobicity of biochar, it could explain the differences in release dynamics between NshBC and SprBC (**Fig 23**). This is because the release of retained NO_3^--N is reliant on continuous water column, which can be difficult to achieve due to hydrophobicity. All our observations are consistent with the pyrolysis continuum hypothesis (**Fig 7**, Masiello 2004, Hammes et al. 2008) suggesting that NO_3^--retention is dependent on material properties and vary between different biochar materials. Future studies should investigate the how production temperature and feedstock impact internal pores and hydrophobicity and their effect on NO_3^--retention.

4.2.4 NITRATE RETENTION AND PLANT GROWTH

Our hypothesis was that NO_3^--retention by biochar does not hinder plant growth, despite its potential to restrict soil N_2O emissions (**H7**). Plant growth was studied as part of the Qvidja field experiment (**II**, **III**) as well as the subsequent but unrelated growth experiment (**IV**).

The plant biomass collected from the biochar amended plots (**II**) was, on average 28–75% and 24–56% higher than the biomass in the fertilized control plots. No statistical differences were observed in root biomass. However, the variation in root biomass appeared to be associated with soil properties, particularly compaction. Consequently, all of the WilB-amended plots suffered from compac-

tion as indicated by significantly higher BD (**Fig 9A**). Indeed, there was a negative but insignificant relationship between the root biomass and BD (not shown) although BD was lower than the threshold often considered to inhibit root growth (Weil & Brady 2017). It is also possible that higher availability of nutrients in the amended plots reduced the need for the plants to grow extensive root systems. Other differences in biomass growth between replicate blocks were associated with soil moisture and temperature. Consequently, replicate block 1 had a greater WHC, which may have contributed to more abundant plant biomass, while taller vegetation and greater water content likely contributed to lower soil temperatures (Rodskjer et al. 1989, Song et al. 2013). However, the only significant differences between biochar treatments and control treatments was in the fraction of leaves and stems, which was larger in SprB (**Fig 24B**).

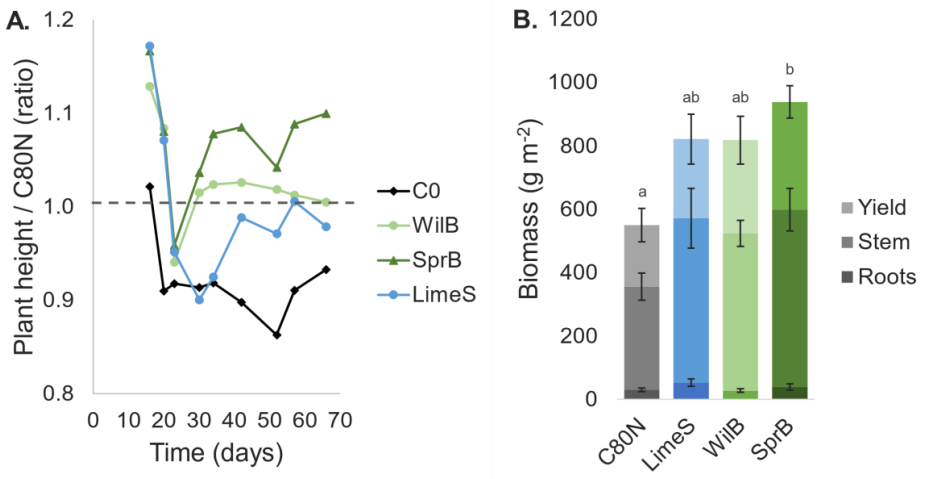

Figure 24 **A**) Plant height compared to control (C80N) during the field experiment (**II**) at Qvidja as well as **B**) root, shoot biomass, and yield parameters after the experiment. No statistical differences were observed with root or yield parameters. Statistical differences (p<0.05) are shown using uppercase letters for yield and root biomass and lowercase letters for stem biomass. For abbreviation see **Table 5**.

During the growth experiment (**IV**), plant height was not significantly affected by fertilization rate (p>0.05), but it was affected by application rate and type of biochar (p<0.05). The biochar treatment with 10% SprBC + 80N had the highest plant growth, and the biochar treatment with 10% NshBC + 140N had the lowest (**Fig 25**). The NshBC treatments had the lowest root and shoot biomass, while the control treatment with 140N fertilization rate had the largest root biomass (**Fig 25**). The largest shoot biomass was observed with 10% SprBC + 140N (**Fig 25**).

Fertilization had little effect on plant growth during the growth experiments (**IV**), indicating that N-availability was not the growth-limiting factor during the experiment. Instead, the plants exhibited blotched shoot tips indicating water stress despite regular watering, likely due to the extremely hot weather in 2021.

The biochar treatments did not alleviate water stress despite their high WHC. This was likely due to quartz sand, which was chosen as an inert growth medium, but together with the biochar particles it formed a very densely packed growth medium, which retained water efficiently but had limited aeration. This may have caused stunted growth in the biochar treatments (**Fig 25**). Future studies should therefore consider the physical properties of the growth medium to avoid this issue.

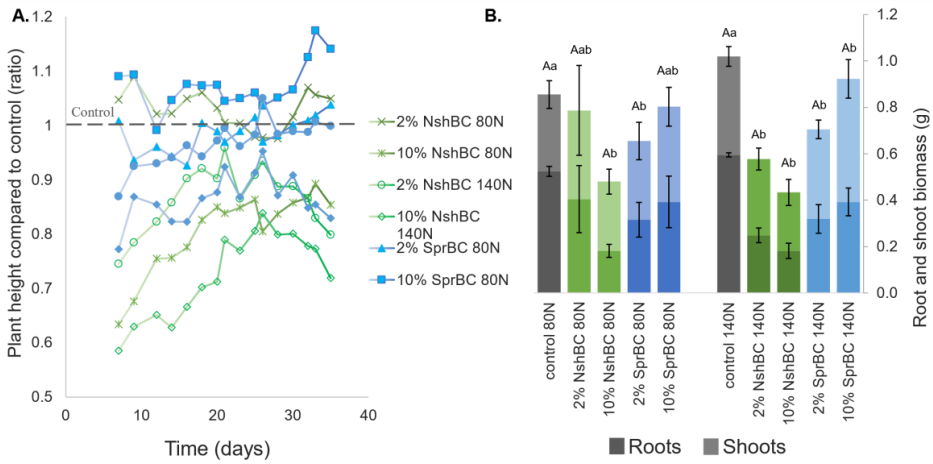

Figure 25 Plant height during the growth experiment (**IV**) compared to control treatments (left) as well as root and shoot biomass (right) after the experiment. Treatments included two fertilization rates (80N and 140N) with two application rates (2% and 10%). No statistical differences were observed with shoot biomasses. Statistical differences (p<0.05) are shown using uppercase letters for shoot biomass and lowercase letters for root biomass. Error bars represent standard deviation (N=3). For abbreviation see **Table 5**.

5 CONCLUSIONS

In this synthesis, I evaluated the impacts of several ligneous soil amendments on soil physico-chemical properties associated with soil fertility and soil GHG exchange. My aim was to address the following gaps in the current literature: 1) lack of long-term field experiments; 2) lack of experiments conducted in boreal climate zone; and 3) lack of experiments conducted with fine-textured, moderately fertile post-glacial soils. My main findings were:

Carbon sequestration potential

The investigations showed (**I**, **II**, **III**) that the use of ligneous soil amendments can be used as a safe option for C sequestration. However, the recovery rates of different ligneous materials can vary considerably depending on several factors, such as chemical composition, particle size, soil texture, climate, and soil management. Based on the available sources, it can be estimate that approximately 40 to 80% of the applied biochar- or lignocellulose-derived C can persist in the managed soil layer after 2 years, and likely much longer.

Effects on soil structure

Cultivated boreal clay soils exhibit aggregated soil structure and high WHC, but they often suffer from anaerobic conditions due to high water tables. When applied to such soils, ligneous soil amendments often reduce BD (**I**, **II**), but rarely impacts the overall soil structure (**I**), which is maintained by tilling operations. Consequently, the long-term effects of the soil amendments on soil structure and WHC are restricted to the pore sizes related to the internal pores of biochar particles (**I**). These internal pores are similar to textural pores that are already dominant in clay soils, meaning that incorporating biochar into the soil does not usually improve soil properties but instead raises the soil particle volume. However, when combined with tillage operations, adding ligneous soil amendments may be beneficial for promoting good soil structure (**II**), either because of the high number of bivalent cations found in the ligneous materials, because of short-term stabilization of soil aggregates due to the decomposition of labile C compounds, or because of irregular shape and size of the amendment particles applied to soil. Nevertheless, it is unlikely that a single application of ligneous soil amendments to boreal clay soils will yield significant benefits to soil structure that would lead to higher crop yields, particularly as the effects of the soil amendments are likely to diminish over time, as more of the ligneous material is decomposed or translocated away from the top soil layer.

Effects on soil acidity

The alkaline properties of ligneous soil amendments have been observed to have a significant liming effect, though the effects have often been temporary. Our research shows that all of the soil amendments when applied to soil at a rate of 2% (w/w) increased soil pH by a minimum of 0.4 units (**I**). The magnitude of

the liming effect was positively correlated with the base cation content of the ligneous materials, but not with their SSA or apparent recovery rates (**I**). This suggests that the liming effect was mainly caused by the alkaline salts present in the ligneous materials, such as carbonates or (oxy)hydroxides. Additionally, the large amount of base cations in the amendments may have mitigated soil acidification by reducing the proportion of H^+ and Al^{3+} ions in soil. These findings may help to clarify some of inconsistent results in previous studies, and future research should investigate how soil amendments impact soil CEC and base saturation.

Effects on soil GHG exchange

The studied ligneous soil amendments did not have significant long-term effects on soil CO_2 emissions (**I**, **II**) and the effects on total N_2O emissions were mainly observed under high moisture conditions (**I**, **II**). However, the findings suggests that the ligneous soil amendments affect soil N_2O emissions triggered by drying and rewetting of the soil (**I**). Specifically, the ligneous soil amendments appeared to mitigate the effects of soil drying on soil microbes. Nevertheless, the total N emissions are ultimately limited by the availability of appropriate C and N substrates, so the overall emissions remained unchanged. Additionally, the reduction of N_2O emissions due to willow biochar was potentially due to local soil compaction, which increased denitrification and led to an increase in the conversion of N_2O to N_2 without any overall reduction in N-losses. These results suggest that previous studies that estimated GHG emissions based on periodic measurements may have overestimated the potential of ligneous soil amendments to reduce GHG emissions (**I**). To gain a deeper understanding of how ligneous soil amendments affect soil N_2O exchange, would require experiments that can quantitatively measure N fluxes between the soil and the atmosphere.

According to our findings, there was a strong correlation between soil pH and the pH of the lignocellulosic materials used, and the differences in N_2O emissions were directly related to these pH levels (**I**). The apparent recovery rates of the materials and other soil parameters did not show any significant correlation (**I**). Therefore, we can conclude that the effect on N_2O emissions was not specific to any particular type of soil amendment such as pulp sludge or biochar, but rather, was due to their ability to influence crucial soil properties such as pH and moisture content.

Effects on nitrate retention

Most of the biochar materials showed the potential to retain NO_3^--N, although in some cases retention was not apparent because of other factors that may have affected soil N dynamics (**I**). Regardless, it was clear that the dynamics of NO_3^- retention varied among biochar materials (**III**, **IV**), possibly due to differences in production temperature and, to a lesser extent, feedstock. Our findings suggest that the standard method for determining mineral-N likely underestimates the N content of biochar-amended soils. Pulp sludge did not have an effect on mineral-N levels.

Despite higher mineral-N contents in spruce biochar-amended soil, there were no observed increases in N_2O emissions under field (**II**) or laboratory conditions (**I**), indicating that retained NO_3^--N is not readily available to microorganisms. However, when plants were grown in biochar-amended growth medium, there was no evidence of N deficiency, and in some cases, more N was available for plants (**II**, **IV**). Nevertheless, the effects on plant growth were often limited, suggesting that N availability was not the growth-limiting factor in our experiments.

Final words

Overall, the results suggest that incorporating ligneous soil amendments into boreal clay soils can have some positive effects on soil fertility, such as increasing C sequestration and soil pH. Moreover, no negative effects on greenhouse gas emissions were observed, which encourage their use as external inputs of C and nutrients into the soil system. However, due to the already fertile nature of these soils, the benefits for plant growth were often limited. Furthermore, the soil processes that I have presented in my work are complex and change slowly. Therefore, I cannot hope to provide definite answers within the scope of this single thesis. Still I hope that I have been able to provide the reader with a sense of understanding of the different mechanisms that are at the heart of sustainable soil management and that this will pave the way for further research into the topic of ligneous soil amendments.

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