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LONG-TERM EFFECTS OF BIOCHARS AS A SOIL AMENDMENT IN BOREAL AGRICULTURAL SOILS

Doctoral Thesis

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ACADEMIC DISSERTATION

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The publications are referred to in the text by their Roman numbers.

CONTRIBUTIONS

The following table presents the contributions of the authors to the original articles of the dissertation:

Publication	Planning of the experiments	Conducting the experiment and data collection	Data Analysis	Writing
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ABSTRACT

Biochars are highly stable porous carbon-rich substances that, when added to soils, have high potential to increase soil carbon (C) sequestration, enhance soil fertility and crop yield, as well as bring other environmental benefits such as reducing emissions of greenhouse gases (GHG) and leaching of nutrients, and remediation of soils contaminated with heavy metals. The potential of biochars to provide agricultural and environmental benefits had led to an exponential increase in the number of studies on the effects of biochars since the beginning of this century. However, the long-term effects of a single application of biochars are not well known. In addition, the beneficial effects of biochars have been observed mostly in (sub-) tropical regions dominated by highly weathered, nutrient-poor acidic soils with low C contents. On the other hand, only a few studies have been conducted on boreal soils that typically have higher C contents. Therefore, this research aimed to investigate the long-term effects of wood-based biochars when combined with different fertilizers in boreal agricultural soils, in terms of i) plant growth and nutrient uptake, ii) soil physical properties, iii) nitrogen (N) dynamics, and iv) GHG emissions. For this, data were collected from four field experiments in Finnish soils, where biochars were applied two to eight years prior to this research, as well as from a greenhouse experiment.

Over the eight years of field experiments, the biochars had minor effects on plant growth and nutrient uptake in both nutrient-poor and nutrient-sufficient soils. Throughout this period, the biochars increased plant growth only on two occasions. On both occasions, the fields were cropped with nitrogen-fixing plants in the previous growing season, thus suggesting that the result may be explained by pre-crop effects. The biochars notably increased plant potassium (K) uptake while reducing plant aluminum (Al) and sodium (Na) uptake, indicating that biochars can ameliorate plant K deficiency, and reduce Al and Na toxicity stress. The biochars increased the contents of several nutrients in plant biomass with time, suggesting a possible long-term fertilization effect either through the slow release of nutrients initially contained in biochars or *via* the enhanced nutrient holding capacity of biochars as they weather in the field. On the other hand, the biochar reduced plant manganese (Mn) content with time in a nutrient-poor soil, suggesting that immediately after application, the biochar increased plant availability of Mn (either present in the biochar or soil), which decreased over the years.

After six or seven years of application, the biochars did not affect the physical or hydrological properties of topsoil. Immediately following the application, the biochar had increased plant available water in coarse-

textured soil. However, this effect disappeared with time, which could be caused by the loss of the biochar or the movement of biochar down the soil profile.

The biochars were shown to have nitrate (NO_3^-) retaining capacity in both the short-term greenhouse experiment and in the field experiment in clayey soil where spruce and willow biochars were applied two years before. The increased N use efficiency, increased plant N uptake, and reduced N leaching by biochars in these experiments were most likely due to the increased retention of NO_3^- by the biochars. The spruce biochar was better than the willow biochar in NO_3^- retention, most likely because of the higher specific surface area. The ^{15}N labeling greenhouse experiment suggested that biochars could induce ammonia volatilization that leads to the loss of fertilizer ammonium (NH_4^+) because of increased soil pH. On the other hand, the ability of biochars to retain NO_3^- increases the soil retention and plant uptake of NO_3^-. Furthermore, there was an indication that biochars increased the plant N availability *via* increased mineralization of soil organic N in the short-term.

The biochars increased carbon dioxide (CO_2) efflux from two out of the four field experiments. In addition to the increased soil microbial activity, the increased plant growth might have contributed to increased CO_2 efflux. However, there were no clear effects of biochars on the emissions of nitrous oxide (N_2O) and methane (CH_4) in any of the fields. Despite this, the spruce and willow biochars tended to reduce N_2O emission during the peak emission period after two years. The potential of biochars to reduce N_2O emission appeared to be dependent on soil silt content and initial soil C content. Interestingly, the wood-based biochar reduced the yield-scaled emissions of non-CO_2 GHG in the field experiment on coarse-textured soil, even after seven years of application. The reduction was mostly due to the increased crop yield, which could be a result of the increased availability of plant water by biochar during the extremely dry growing season.

Overall, no negative effects of biochars were observed in the greenhouse or the longer-term field experiments in boreal soils. Therefore, this research supports the concept that biochars as soil amendment materials are a safe and practical way to increase soil C sequestration. However, achieving consistent noticeable agronomic and other environmental benefits after several years of a single application of wood-based biochars is implausible in boreal soils. Thus, subsequent application of nutrient-rich biochars, such as co-composted biochars likely provides a more reasonable alternative for a consistent increase in soil C sequestration, as well as agronomic benefits. Future biochar research should focus on this direction.

ABBREVIATIONS

AGB	Aboveground Biomass
ANOVA	Analysis of Variance
CEC	Cation Exchange Capacity
CFE	Chloroform Fumigation Extraction
DOC	Dissolved Organic Carbon
EBC	European Biochar Certificate
FTIR-TGA	Fourier Transform Infrared – Trace Gas Analyzer
GHG	Greenhouse Gases
GHGI	Greenhouse Gas Intensity
GWP	Global Warming Potential
HELCOM	Helsinki Commission
IBI	International Biochar Initiative
ICP-OES	Inductively Coupled Plasma – Optical Emission Spectrometry
IPCC	Intergovernmental Panel on Climate Change
IRMS	Isotope Ratio Mass Spectrometer
MBC	Microbial Biomass Carbon
MBM	Meat Bone Meal
MBN	Microbial Biomass Nitrogen
PAH	Polyaromatic Hydrocarbons
PVC	Polyvinyl Chloride
RCBD	Randomized Complete Block Design
SOC	Soil Organic Carbon
SOM	Soil Organic Matter
TN	Total Nitrogen
UNFCCC	United Nations Framework Convention on Climate Change
WHC	Water Holding Capacity
WRC	Water Retention Curve
w/w	weight to weight
w/v	weight to volume

KEY DEFINITIONS

Biochar: a product of heating biomass in the absence of or with limited air to above 250°C, a process called charring or pyrolysis. Biochar is different from charcoal or other carbon products because of its intended use for soil application or broader environmental management (Lehmann and Joseph, 2015).

Carbon sequestration: the process of transferring and securing storage of atmospheric CO_2 into other long-lived C pools that would otherwise be emitted or remain in the atmosphere. Carbon sequestration may be a natural or human-driven process. The aim of human driven carbon sequestration is to balance the global carbon budget such that future economic growth is based on a carbon neutral strategy of no net gain in the atmospheric carbon pool (Lal, 2008).

Soil amendment: any material that improves soil physical, chemical, and biological properties when added to soil, which upgrades the conditions for plant growth.

Sustainable agriculture: focuses on the need to develop agricultural technologies and practices that: i) do not have adverse effects on the environment, ii) are accessible to and effective for farmers, and iii) lead to both improvements in food productivity and have positive effects on environmental goods and services. Sustainability in agricultural systems incorporates both resilience (the capacity of systems to buffer against shocks and stresses) and persistence (the capacity of systems to continue over long periods), and addresses many wider economic, social, and environmental outcomes (Pretty, 2008).

1 INTRODUCTION

1.1 BIOCHARS AS TOOLS FOR MITIGATING CLIMATE CHANGE AND INCREASING AGRICULTURAL SUSTAINABILITY

The anthropogenic GHG emissions have been unprecedentedly increasing in the atmosphere since the mid-20th century, leading to the warming of the climate with widespread adverse impacts on human and natural systems (IPCC, 2014). Therefore, the urgent need for timely GHG emission mitigation strategies and actions has been highlighted. In 2015, the United Nations Framework Convention on Climate Change (UNFCCC) Paris Agreement established the goal to maintain global warming below 2°C, and pursue efforts to limit it to 1.5°C, above pre-industrial levels (UNFCCC, 2015). Achieving this goal requires substantial reductions of GHG emissions along with the sequestration of CO_2 from the atmosphere, creating a net negative emissions scenario (Field and Mach, 2017; Seneviratne et al., 2018). The capture of CO_2 from the atmosphere into plant biomass via photosynthesis, and eventually pyrolyzing the plant biomass into highly stable biochar has received considerable interest as an effective means to sequester C and thus mitigate climate change (Lehmann et al., 2006; Kuzyakov et al., 2014; Lehmann and Joseph, 2015; Lehmann et al., 2021). Woolf et al. (2010) estimated that widespread application of biochars could offset a maximum of 12% of the current anthropogenic GHG emissions (i.e. 1.8 Pg CO_2-C_e per year of the 15.4 Pg CO_2-C_e emitted annually). A recent study estimated an even higher reduction in global GHG emissions of 3.4–6.3 Pg CO_2-C_e using biochars (Lehmann et al., 2021). Apart from that, biochars can reduce the mineralization of soil organic matter (SOM) i.e. negative priming effect (Weng et al., 2017; Blanco-Canqui et al., 2020; Chen et al., 2021), which further underscores the C sequestering potential of biochars.

Despite the increase in agricultural productivity, modern agricultural practices including increased use of chemicals has caused detrimental environmental and ecological problems (Tilman, 1999). The applied fertilizers intended to enhance crop production can also exacerbate GHG emissions and eutrophication of waterways. For instance, during 2000–2014, the application of synthetic N fertilizer into agricultural soils accounted for approximately 70% of the total global emissions of N_2O, which has a global warming potential (GWP) 298 times higher than CO_2 (Xu et al., 2020). Similarly, the N load to water bodies is of great concern; agriculture has been identified as a major contributor of the total N load to the Baltic Sea, contributing 46% of the total N load (HELCOM, 2018). Therefore, there is an urgent need for sustainable agricultural practices that enhance agricultural production and simultaneously reduce the environmental consequences. Agricultural sustainability focuses on the need to develop technologies and practices that do not have adverse effects on environmental goods and services, are accessible to and effective for farmers, and lead to improvements in food productivity (Pretty, 2008). Because biochars are simple substances that can be produced easily with simple technologies from simple available materials, and their application in soils can bring positive agronomic benefits and reduce negative environmental effects of agriculture, the application of biochars as soil amendment materials has great potential as a tool for sustainable agriculture.

Biochars are carbonaceous porous materials produced by thermochemical conversion of biomass in an oxygen-limited environment (pyrolysis). The interest in using biochars as a soil amendment method as a strategy for mitigating global climate change and enhancing agricultural productivity has been growing intensively since around 2000 (Wu et al., 2019a; Joseph et al., 2021). It was encouraged by the earlier studies on Terra Preta (literal meaning "black soil"), the dark and highly fertile anthropogenic soil in the Amazon region (Smith, 1980). Historic application of charred materials in these soils was found to be responsible for high soil organic matter contents and soil fertility, as well as contributing to mitigating climate change (Glaser et al., 2002; Lehmann et al., 2006; Mao et al., 2012).

1.2 PRODUCTION OF BIOCHARS

Biochars can be produced by pyrolyzing a wide range of organic raw materials, but mainly wood chips, agricultural residues or manure are used. Biochars can be produced on a large industrial scale along with other valuable products – bio-oil and syngas. These products, along with the generated heat, could be used for fulfilling energy demands such as heating buildings (Lehmann, 2007). However, the cost of the commercially produced biochars might not be affordable for farmers [e.g. 700–800 euros per ton in Finland (Salo, 2018)], especially in developing countries. Alternatively, biochars can be produced at a local scale using low-cost brick, earth-mound, metal, and pit kilns from locally available raw materials (Schmidt and Taylor, 2014; Mia et al., 2015; Pandit et al., 2017). These low-cost kilns are easy to build and operate by farmers, and can produce high-quality biochars that meet European Biochar Certification (EBC) and International Biochar Initiative (IBI) certification (Cornelissen et al., 2016).

Based on the residence times and purpose, pyrolysis systems can be categorized into slow pyrolysis, fast pyrolysis, and gasification (Brewer et al., 2009). In slow pyrolysis, the feedstock is heated slowly at the rate of 1–20°C min^{-1} in the absence of oxygen for a long period, ranging from five minutes to multiple hours. Biochar is the main product of slow pyrolysis. In fast pyrolysis, the dry feedstock is heated up very rapidly up to 1000°C for a short time, then quenched to maximize the production of bio-oil. In gasification, the feedstock is heated at a higher temperature, with the introduction of some oxygen to produce non-condensable syngas rich in H_2 and CO_2.

1.3 STABILITY OF BIOCHARS

The presence of a high proportion of aromatic C rings resists the biological and thermochemical degradation of biochars (Lehmann and Joseph, 2015). Because of this, biochars can persist in soil for hundreds to several thousands of years (Kuzyakov et al., 2014; Joseph et al., 2021). The potential of biochars to sequester C depends on the persistence of biochars in soil, which mainly depends on the properties of biochars, determined by the feedstock and pyrolysis conditions (Spokas, 2010; Wang et al., 2016a; Joseph et al., 2021). For example, wood-derived biochars have a slower decomposition rate compared to crop, grass or manure-based biochars because of the presence of a higher proportion of aromatic carbon (Singh et al., 2012; Kuzyakov et al., 2014; Singh and Cowie, 2014; Wang et al., 2016a). Similarly, a higher pyrolysis temperature (>450°C) favors the production of biochars with a higher portion of aromatic C, increasing their recalcitrance and thus persistence in soils (Crombie et al., 2013; Wang et al., 2016a). The elemental ratios $H:C_{org}$ and O:C provide robust indicators of biochar stability (Spokas, 2010; Enders et al., 2012). During pyrolysis, H and O elements are depleted and biochars become rich in C-content, hence the increase in pyrolysis temperature decreases H:C and O:C ratios (Lee et al., 2013). Notably, $H:C_{org}$ values higher than 0.7 are not considered as biochar according to IBI standards (Enders et al., 2012; IBI, 2012; Leng et al., 2019). An O:C value of less than 0.2 indicates a minimum biochar half-life of 1000 years (Spokas, 2010).

In addition, the stability of biochars also depends on edaphic and climatic factors. For instance, the decomposition rate of biochars is usually lower in soils with higher clay content (Wang et al., 2016a) and with clay minerals such as kaolinite and sesquioxides that favor the formation of stable aggregates (Joseph et al., 2021), since the occlusion of biochars into soil aggregates limits their accessibility to decomposing microbes. On the other hand, biochars in soil could be prone to mineralization at higher ambient temperatures due to increased oxidation of biochar particles in addition to increased microbial decomposition (Nguyen et al., 2010; Fang et al., 2014).

1.4 AGRICULTURAL AND ENVIRONMENTAL EFFECTS OF SOIL APPLICATION OF BIOCHARS

1.4.1 EFFECTS OF BIOCHARS ON PHYSICAL, CHEMICAL, AND BIOLOGICAL PROPERTIES OF SOILS

Biochars are porous materials containing large surface areas with negative charges (Banik et al., 2018). Leng et al. (2021) reported that the total pore volume and specific surface area of normal biochars reported in recent studies ranged from 0.016–0.083 $cm^3\ g^{-1}$ and 8–132 $m^2\ g^{-1}$, respectively. However, depending on the pyrolysis conditions and post-treatments, the pore volume and specific surface area of biochar can be as high as 1.77 $cm^3\ g^{-1}$ and 3263 $m^2\ g^{-1}$, respectively (Liu et al., 2016). The application of such porous biochars to soil generally increases soil porosity and reduces soil bulk density (Burrell et al., 2016; Blanco-Canqui, 2017; Razzaghi et al., 2020). Biochars produced from wood or at higher pyrolysis temperatures typically have higher specific surface area and porosity than biochars produced from manure or sludge, or at lower pyrolysis temperatures (Ippolito et al., 2020; Tomczyk et al., 2020).

Depending on the surface properties of biochars, they can also interact with soil particles, e.g. through the formation of organo-mineral complexation *via* cation bridging, which can enhance soil aggregate stability (Soinne et al., 2014; Ma et al., 2016; Blanco-Canqui, 2017; Heikkinen et al., 2019). The increased soil aggregate stability further helps to enhance the accumulation of soil organic carbon (SOC) content (Zhang et al., 2017). Biochars may enhance soil water holding capacity (WHC) by direct absorption of water into their pores (Rasa et al., 2018) and by changing soil aggregation or soil porosity (Yoo et al., 2014). The increased water retention after application of biochars is usually readily plant available (Peake et al., 2014; Głąb et al., 2016; Rasa et al., 2018; Razzaghi et al., 2020), which may facilitate plant tolerance to drought stress.

The improvement in soil physical properties after the application of biochars is usually observed more clearly in coarse-textured soils than in fine-textured soils (Blanco-Canqui, 2017; Atkinson, 2018; Razzaghi et al., 2020). However, some studies reported no effects of biochars on soil physical and hydrological properties, even at higher application rates in coarse-textured soils. For example, Hardie et al. (2014) did not find any effects on soil physical or hydrological properties after the application of acacia biochar at the rate of 47 t ha^{-1} to a loamy sand soil. Similarly, Jeffery et al. (2015) observed that the physical and hydrological properties in coarse sand soil were not affected by the application of biochars produced from grass hay at 400°C and 600°C at different rates from 1 to 50 t ha^{-1}. They attributed the lack of effects to the hydrophobicity of biochars. Heikkinen et al. (2019)

reported that the hydrophobic nature of biochars arises due to non-polar alkyl functional groups at their surface. The hydrophobic surface prevents water from entering the internal pore structure of biochars, which prohibits an effect on soil water retention even though they have porosities that can potentially enhance water retention (Jeffery et al., 2015; Heikkinen et al., 2019). In addition, biochars have been reported to be less effective in retainining water in soils with high initial SOC, which already have high water holding capacity (Abel et al., 2013).

The addition of biochars can alter the chemical properties of soils such as soil pH, cation exchange capacity (CEC), and contents of plant nutrients, such as N, P, K, Ca, and Mg. Biochars are usually alkaline because of their ash contents (containing carbonates and hydroxides of alkali metals e.g. Na, K, and alkaline earth metals e.g. Ca, Mg) and basic functional groups on their surfaces, which increase with higher pyrolysis temperatures (Suliman et al., 2016; Zhao et al., 2017; Gezahegn et al., 2019). Therefore, the addition of biochars has the potential to increase soil pH and ameliorate soil acidity (Aamer et al., 2020; Kannan et al., 2021; Ginebra et al., 2022). The liming capacity of biochars in soil correlates with biochar pH (Gezahegn et al., 2019). However, some high-pH biochars may have low liming capacity ($CaCO_3$ equivalent) and might not affect soil pH (Tammeorg et al., 2014a; Tammeorg et al., 2014b). The actual ability of biochars to increase soil pH also depends on soil buffering capacity.

The surfaces of biochars contain negative charges because of the deprotonation of oxygen-containing functional groups such as carboxylic (-COOH) and phenolic groups (-C-OH) (Banik et al., 2018; Tan et al., 2020). These negative surfaces, along with adsorption of highly oxidized organic matter on the surfaces of biochars, can increase the CEC of soils (Liang et al., 2006). The increase in soil pH after the addition of biochars or ash contained in biochars may increase soil CEC (Tan et al., 2020). The ability of biochars to increase soil CEC is a key property, because it affects the retention of nutrients and regulates a wide range of biogeochemical processes in soils. Therefore, biochar surface oxygenation as a post-treatment to enhance CEC has been gaining attention (Huff et al., 2018; Kharel et al., 2019).

Biochars also add plant nutrients to the soil, but the amount of nutrients depends on the feedstock and pyrolysis conditions (Ippolito et al., 2020). Similarly, the potential of biochars to alter overall chemical properties also depends on the feedstock and pyrolysis conditions. Manure and sewage-based biochars typically have greater pH, CEC, and nutrient input (N, P, K, Ca, Mg) to the soil compared to the crop residue and wood-based biochars (Ippolito et al., 2020; Tomczyk et al., 2020). An increase in pyrolysis temperature (>300^{o}C) increases the ash contents that contain hydroxides and carbonates, which help to increase biochar pH (Ippolito et al., 2020). However, the CEC of biochars decreases with an increase in pyrolysis temperature (>400°C), because at high temperatures, the negative surface charge decreases due to the appearance of more organized C layers with fewer contents of functional groups (Banik et al., 2018; Tan et al., 2020; Tomczyk et al., 2020).

The changes in soil physical and chemical properties after the addition of biochars – both directly and indirectly – affect the composition and function of microorganisms in soils, and *vice versa,* which consequently may affect the agronomic and environmental effects of biochars (Lehmann et al., 2011; Xu et al., 2016a; Zhang et al., 2018). In the short-term, biochars affect soil microbial activities mainly by providing labile carbon substrate, whereas the long-term effects are related to modification of the soil ecological niche (Hardy et al., 2019). The effects of biochars on soil microorganisms depend on both the biochar and soil types. For example, in a meta-analysis, Zhang et al. (2018) reported that low pyrolysis temperature-produced biochars significantly increased the soil fungi:bacteria ratio, most likely due to enhancement of nutrients and soil pH. In the same study, they claimed that an increase in soil microbial activities is more pronounced in low nutrient-containing fine or coarse-textured soils after the addition of biochars. Similarly, Pokharel et al. (2020) stated that microbial biomass carbon and enzyme activities were higher with biochars produced at relatively low pyrolysis temperatures (300–500°C) with high pH (>10) and low C:N ratio (< 50), and when applied to the fine-textured acidic soils with low C and N contents.

Biochars can enhance the abundance of arbuscular mycorrhiza (Yang et al., 2020a) and ectomycorrhizal fungi (Verma and Reddy, 2020) that could assist plants with the uptake of nutrients and water. In addition, biochars can also influence microbial community structure and activities that affect C and N cycling. For instance, the addition of biochars favors the growth of microbes, thus increasing microbial biomass (Lehmann et al., 2011; Pokharel et al., 2020). The increase in microbial biomass is mainly attributed to the presence of some labile C (≤1% of total mass) in biochars (Cross and Sohi, 2011). In the short-term, the increased microbial growth after the addition of biochars could enhance the priming effect, i.e. stimulation of SOC mineralization (Zimmerman et al., 2011; Singh and Cowie, 2014) and N immobilization into microbial biomass (Bruun et al., 2012; Tammeorg et al., 2012; Borchard et al., 2014). However, with time, biochars increase organo-mineral interactions protecting SOC from microbial decomposition (Zimmerman et al., 2011; Singh and Cowie, 2014; Maestrini et al., 2015; Wang et al., 2016a; Weng et al., 2017), and mineralization of nitrogen (Mia et al., 2017; Ding et al., 2022). Furthermore, Xiao et al. (2019) reported in their meta-analysis that biochars notably increased the abundance of ammonia-oxidizing archaea and denitrification genes (nirS, nirK, and nosZ), consequently affecting the N cycling.

1.4.2 EFFECTS OF BIOCHARS ON PLANT GROWTH

Biochars can enhance plant growth by acting as a liming agent (Van Zwieten et al., 2010; Cornelissen et al., 2018), increasing the water-holding capacity of soils (Karhu et al., 2011; Uzoma et al., 2011; Batista et al., 2018), retaining the applied nutrients (Uzoma et al., 2011; Oladele et al., 2019), and acting as a source of nutrients (Kloss et al., 2012; Wang et al., 2016b; Ippolito et al., 2020). Therefore, the effectiveness of biochars in enhancing crop productivity has been well documented in several recent meta-analyses (Jeffery et al., 2011; Biederman and Harpole, 2013; Liu et al., 2013; Jeffery et al., 2017a; Liu et al., 2019a; Dai et al., 2020; Ye et al., 2020; Zhang et al., 2020a). However, negative effects on plant growth have been reported as well. For example, Kammann et al. (2015) found that 2% of wood-based fresh biochar reduced plant growth, especially in N-limited condition, most likely because of the reduced plant availability of nitrate and other nutrients retained by the biochar. Similarly, Xu et al. (2016b) reported that biochar promoted a phosphate precipitation/sorption reaction that decreased plant P availability, which consequently led to reduced plant yield in saline-sodic soil.

The feedstock and pyrolysis temperature affect the plant response to biochars. Manure-based biochars usually have a higher CEC (Pariyar et al., 2020) and nutrient contents such as N and P than wood-based biochars (Ippolito et al., 2020). As a result, the application of manure-based biochars often results in positive plant responses (Biederman and Harpole, 2013; Liu et al., 2013). Similarly, an increase in pyrolysis temperature produces biochars with high pH, surface area, porosity, and ash contents, but with low CEC and volatile matter content (Lee et al., 2013; Zhao et al., 2018; Tomczyk et al., 2020). High ash content in biochars represents the availability of high nutrient contents that might elicit a positive plant response (Dai et al., 2020). Moreover, the plant response after the addition of biochars is usually positive in nutrient-poor, low initial SOC content (<20 g kg^{-1}), sandy and acidic soils (Liu et al., 2013; Ye et al., 2020).

1.4.3 EFFECTS OF BIOCHARS ON SOIL GHG EMISSIONS

Biochars also have the potential to reduce the emissions of GHG such as CO_2, CH_4, and N_2O from soils, which further highlights their role in mitigating climate change. As mentioned in Section 1.4.1, the presence of labile C in biochars may enhance short-term microbial activity and thus increase soil CO_2 emissions, but in the long-term, biochars favor negative priming and thus decrease soil CO_2 emissions. In support of this, Ginebra et al. (2022) found that in a field experiment, wood-based biochar and poultry litter carbonaceous material increased CO_2 flux during the first 45 days after application, after which the CO_2 fluxes tended to decrease. Similarly, the recent global meta-analyses by Borchard et al. (2019), Liu et al. (2019a), and

Zhang et al. (2020a) reported that biochars reduced the overall emissions of N_2O by 38% (608 observations from 88 studies), 6–30% (552 observations from 90 studies), and 38% (444 observations from 129 studies), respectively. The ability of biochars to reduce N_2O emissions has been mainly linked to their capability to affect the denitrification process, which is the major process of N_2O production (Case et al., 2015). Biochars can facilitate the reduction of N_2O to N_2 during the last step of denitrification by increasing soil pH, which enhances the synthesis of N_2O reductase or increases N_2O reductase genes (*nosZ*) (Cayuela et al., 2013; Harter et al., 2014; Van Zwieten et al., 2014; Dannenmann et al., 2018). Furthermore, biochars can increase the abundance of N_2O-reducing microbes (Liao et al., 2021a), or may decrease the availability of NO_3^- to denitrifying microbes (Van Zwieten et al., 2014; Kammann et al., 2015; Haider et al., 2016), which will eventually lead to less N_2O emissions. Furthermore, biochars improve soil aeration by reducing anoxic microsites, eventually decreasing denitrification rates and N_2O production (Rogovska et al., 2011). Likewise, in a meta-analysis of 193 observations from 42 studies, Jeffery et al. (2016) concluded that biochars reduced CH_4 emissions (or increased soil CH_4 sink) mostly from flooded (i.e. paddy) fields and/or acidic soils. This reduction could be explained by the increase in methanotrophic bacteria and a decrease in methanogenic archaea after the application of biochars (Qi et al., 2021). In upland soils as well, biochars can increase soil CH_4 uptake followed by methanotrophic oxidation due to increased soil aeration (Karhu et al., 2011).

The response of crop yield and GHG emissions to the addition of biochars should be assessed together with simultaneous assessment of biochar application for mitigating climatic impact and food security. For this purpose, yield-scaled GHG emissions i.e. GHG emissions (CO_2 equivalents) per crop yield, also denoted as greenhouse gas intensity of crop production (GHGI), serves as a good indicator. According to synthesis studies, biochars in general reduce GHGI (Liu et al., 2019b; Zhang et al., 2020a).

1.5 RESEARCH NEEDS FOR AGRICULTURAL USE OF BIOCHARS

1.5.1 NEED FOR LONG-TERM FIELD EXPERIMENTS ON THE USE OF BIOCHARS

Although biochars have potential agronomic and environmental benefits, as elaborated in the previous section, most of these results are based on laboratory, greenhouse, and short-term field experiments; often, they are inconclusive and contradictory (Mukherjee and Lal, 2014; Elbasiouny et al., 2021). This is mainly because the ability of biochars to provide agronomic and environmental benefits depends on the biochar types, application rates, soil properties, and environmental conditions (Cornelissen et al., 2013; Alburquerque et al., 2014; Blanco-Canqui, 2017; Jeffery et al., 2017a; Zhang et al., 2020a). Moreover, any positive effects of biochars may prevail only for the short-term. For instance, Cornelissen et al. (2018) reported that the positive effects of biochar on crop yield due to alleviation of soil acidity faded after a few growing seasons (about one year), indicating the necessity of biochar reapplication. Similarly, Jin et al. (2019) found that over a 5-year field experiment, wheat straw biochar increased rapeseed yield only during the first year, because the positive effect of biochar on soil pH and water availability weakened over time. It is noteworthy that there are currently only a few peer-reviewed publications on the long-term (i.e. more than five years) effects of biochars. The contradictory results from short-term experiments, uncertainty about the effects of biochars in the long-term, and poor mechanistic understanding of the key factors involved point toward the need for long-term field experiments to conclusively ascertain the extent of biochars' ability to generate agronomic benefits.

The aging of biochars in the field has the potential to enhance nutrient holding capacity, because with time, the surface of biochars is oxidized with the formation of more oxygen-containing functional groups (Cheng et al., 2006) that increase cation exchange capacity. In addition, longer interactions of biochars with soils, plant roots, microbes, and root exudates in the field facilitate the development of organic coatings in their surfaces (Hagemann et al., 2017a) that provide an extra layer of porosity or act as glue to withhold more nutrients (Conte and Laudicina, 2017; Hagemann et al., 2017a). Nevertheless, only little is known about how bioavailability and plant uptake of macro- and micro-nutrients change with time as biochars age in the field.

Some studies have suggested that biochars might have limited potential to reduce GHG emissions in the long-term. For example, Spokas (2013) reported that field-aging of biochars diminished their ability to reduce N_2O emissions. Similarly, Thers et al. (2020) reported that N_2O emission was reduced only by fresh biochars, but not field-aged biochars. Furthermore, the meta-analyses by Song et al. (2016) and Borchard et al. (2019) found that the ability of biochars to suppress N_2O emissions was transient. Despite this, biochars can potentially reduce GHG even in the long-term (Wu et al., 2019b). Field-aged biochars may reduce the accessibility of inorganic N to nitrifying or denitrifying microbes due to increased retention of soluble inorganic N in a porous biochar matrix, which contributes to decreasing N_2O emissions (Singh et al., 2010; Haider et al., 2016; Liao et al., 2021b). In the same way, reduced soil bulk density and increased soil aeration by biochars could persist for several years (Burrell et al., 2016; Blanco-Canqui, 2017), favoring methane oxidation over methanogenesis, and thereby reducing CH_4 emissions or increasing soil CH_4 uptake. Furthermore, in the long-term, an increase in inter-particle cohesion by biochars promotes micro-aggregate stability and further stabilizes SOC, eventually decreasing CO_2 emissions (Zimmerman et al., 2011; Singh and Cowie, 2014; Weng et al., 2017). Despite these promising potentials, review articles show that there are only limited number of the long-term field experiments (more than 5 years after biochar application), which report persistent reductions of GHG fluxes by biochars (Song et al., 2016; Liu et al., 2018; Zhang et al., 2020a).

The positive agronomic and environmental effects of biochars are directly related to the improvement of soil physical and hydrological properties by the addition of biochars (Mukherjee and Lal, 2013; Blanco-Canqui, 2017). Since the liming and nutrient addition effects of biochars are usually only short-term in nature, the modification of soil structure by improved soil aggregation (Soinne et al., 2014; Heikkinen et al., 2019) is the most likely cause of any positive effects of biochars in the long-term. In a meta-analysis, Islam et al. (2021) reported that improvement of soil aggregation by biochars became increasingly more significant over a longer time (>3 years). On the contrary, the biochar particles may disappear in the long-term due to mineralization, physical fragmentation, dissolution, and downward movement in the soil profile (Spokas et al., 2014; de la Rosa et al., 2018; Kätterer et al., 2019). Verifying the persistent effects of biochar on soil physical properties requires their assessments in long-term field experiments.

Additionally, the addition of biochars may have negative effects. Biochars produced from suboptimal raw materials and processes may contain concerning levels of polyaromatic hydrocarbons (PAH) and heavy metals, which can have detrimental effects on soil organisms and crops (Kloss et al., 2012). Furthermore, biochars can have other potential adverse effects; they can decrease the plant available water in clay soils, increase erosion and particulate matter emissions due to surface application to sandy soils, increase soil salinity, and decrease soil fertility because of an increase in pH of alkaline soils causing precipitation of nutrients (Brtnicky et al., 2021). Therefore, before the widespread application of biochars as a soil amendment, the potential negative effects of biochars in the long-term should be thoroughly assessed, because once applied in the soil, they are impossible to remove.

1.5.2 NEED FOR BIOCHAR STUDIES IN THE BOREAL REGION

The synthesis of studies exploring the agronomic and environmental benefits of biochars from the global perspective show that biochars can have varying effects at different climatic zones. While most of the biochar studies are conducted in tropical, sub-tropical, and temperate climates (Jeffery et al., 2011; Jeffery et al., 2017a; Liu et al., 2019a; Zhang et al., 2020a), only few are available from boreal regions (see Figure 1). The positive effects of biochar on crop yields are more common in the tropical and sub-tropical zones, where the soils are often more acidic and nutrient-deficient than in the temperate zones (Jeffery et al., 2017a; Liu et al., 2019a). On the other hand, the potential of biochars to reduce N_2O emissions was shown to be higher in the temperate zones than in the tropical and sub-tropical zones (Liu et al., 2019a). However, boreal soils are different because of the typically higher C content (Heikkinen et al., 2021) and periodic freeze-thaw cycles that can increase surface oxidation of biochars, ultimately increasing their adsorption capacity (Wang et al., 2021). Hence, results from other climatic zones may not apply to the boreal zones. The few short-term biochar studies previously conducted in boreal climates reported that biochar had a limited effect on crop yield in the first two to four years (Tammeorg et al., 2014a; Tammeorg et al., 2014b; O'Toole et al., 2018; Soinne et al., 2020). Therefore, it is necessary to investigate the possibility of obtaining long-term agricultural and environmental benefits of biochars in boreal regions.

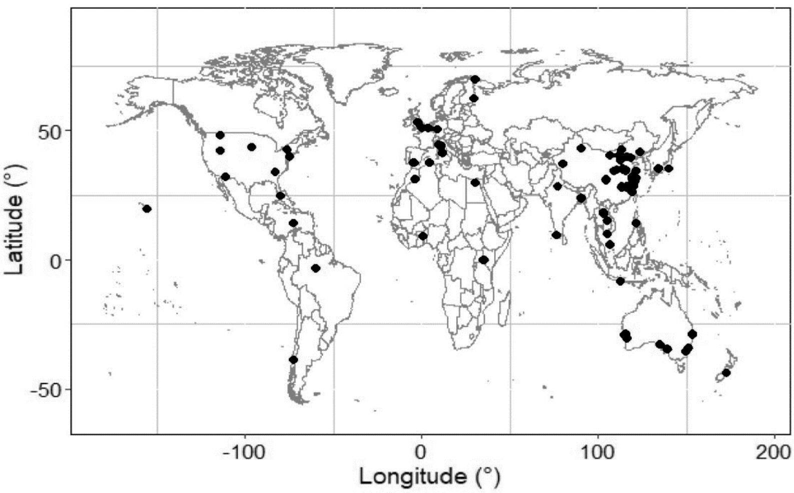

Figure 1. Global distribution of studies investigating the response of crop yield and GHG emissions to biochar application included in the meta-analysis by Zhang et al. (2020a). © Authors. Used under Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

1.5.3 NEED FOR IMPROVING THE FERTILIZER NITROGEN USE EFFICIENCY BY BIOCHARS

The application of fertilizer N is essential for boosting food production and thus contributing to global food security. However, globally, two-fifths of N input is lost to the air and water (Liu et al., 2010), which not only hinders crop production but also threatens ecological balances and functions. Furthermore, it has been estimated that the use of fertilizer N will be doubled or tripled by the second half of the 21st century due to the rapid increase in global food demand (Tilman et al., 2011). The inefficient agricultural management practices can exacerbate soil N losses and consequently accelerate global warming, decrease stratospheric ozone, increase ecosystem eutrophication, and induce the formation of pollutant particulate matter in the atmosphere (Gruber and Galloway, 2008). Therefore, there is an urgent need for sustainable agricultural management practices to enhance N use efficiency such that most of the applied fertilizer N would be taken up by plants or retained in the soil, while the losses of N to air and water would be concurrently diminished.

The application of biochars can influence the soil N cycle (Figure 2) and may have potentially positive effects to increase the soil N retention, decrease leaching and gaseous losses of N, and enhance plant N uptake (Clough et al., 2013; Nguyen et al., 2017; Liu et al., 2018). On the other hand, undesirable effects of biochars on soil N dynamics and plant N availability have been reported in some studies. For instance, Sánchez-García et al. (2014) found increased soil N_2O emissions with the application of biochar due to facilitated nitrification. Similarly, Singh et al. (2010) observed increased nitrate leaching immediately after the application of poultry manure biochar produced at 400°C. These controversial beneficial and undesirable effects of biochars on soil N dynamics reflect the wide variation in the characteristics of biochars and soils (Liu et al., 2018). Moreover, although the mechanisms of how biochars affect the retention of N and soil N effluxes have been postulated (Clough et al., 2013; Brassard et al., 2016; Nguyen et al., 2017), a comprehensive mechanistic understanding of how biochar affects dynamics of soil N still remains elusive because of the complex interaction between soil, biochar and the N cycle (Figure 2).

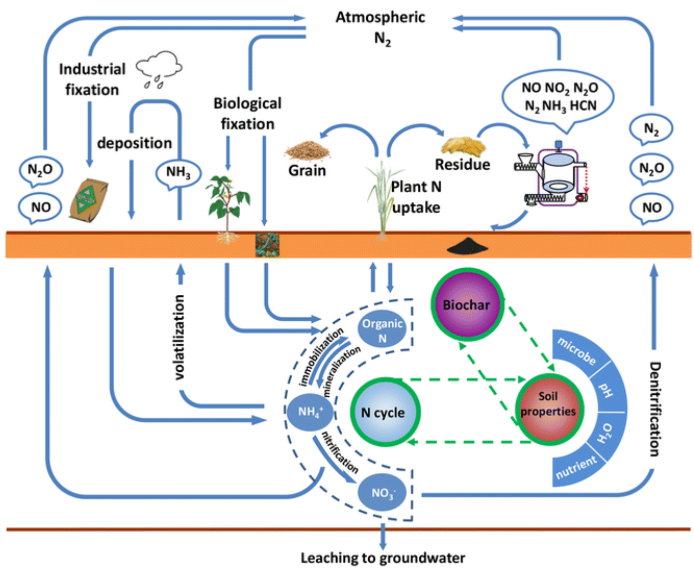

Figure 2. The conceptual impact of biochars on the soil N cycle in biochar-amended soils. Adapted from Liu et al. (2018) with permission from Springer.

Ammonium (NH_4^+) and nitrate (NO_3^-) ions are important reactive species of N in soils. They are accessible for plant uptake, easily leachable (especially NO_3^-), and provide substrates for nitrification and denitrification that produce N_2O as a byproduct. Biochars can affect the fate of NH_4^+ and NO_3^- ions in soils. For example, because of enhanced CEC, biochars can increase the retention of positively charged NH_4^+ ions in soils. The field-aging of biochars is expected to further enhance the retention of NH_4^+ ions (Mia et al., 2017). On the contrary, the increase in soil pH (>7) after biochar addition could increase the loss of NH_4^+ ions via ammonia (NH_3) volatilization (Schomberg et al., 2012). On the other hand, NO_3^- is a highly mobile ion and thus highly susceptible to leaching. Biochars have been reported to have low anion exchange capacity hence they have a limited affinity to adsorb NO_3^- ions (Yao et al., 2012; Gai et al., 2014). However, since biochars can increase water holding capacity (as mentioned in section 1.4.1), they can reduce the leaching of NO_3^- ions (Yoo et al., 2014). Nevertheless, some studies have found that some biochars, particularly when co-composted with nutrient-rich organics, have an extraordinary affinity to retain NO_3^- ions on or in a porous biochar matrix, often described as "nitrate capture" (Kammann et al., 2015; Hagemann et al., 2017a; Hagemann et al., 2017b; Joseph et al., 2018). The formation of organic or organo-mineral complex coatings on the surface of biochars has been found to enhance the retention of nitrate (or nutrients) (Hagemann et al., 2017a; Joseph et al., 2018). Such retention of nitrate has also been observed in biochars aged in the field for a few years (Haider et al., 2016; Haider et al., 2017). The surface oxidation of biochars in the field might facilitate the formation of organic coatings, as observed in the co-composted biochar, favoring NO_3^- retention (Hagemann et al., 2017a). Additionally, the hydrophobic surfaces of fresh biochars may become more hydrophilic after prolonged field exposure because of the formation of hydrophilic functional groups and degradation of tars and other hydrophobic components on the surface of biochars (Rechberger et al., 2017). This enhances the interaction of biochars with water, which improves the retention of NO_3^-. However, NO_3^- may be strongly associated with field-aged biochar pores, which may limit its availability to plants (Haider et al., 2016; Haider et al., 2017).

The ^{15}N tracing technique can be a helpful tool to trace the pathways of NH_4^+ and NO_3^- following their application to soil, and to quantify the effects of biochar on the retention and loss of fertilizer N. This helps to understand or verify the mechanisms of how biochars affect soil N dynamics.

2 AIMS

This research aimed to determine whether a single application of biochar in boreal agricultural soils can increase agricultural productivity and alleviate negative consequences of agricultural practice on the environment in the long-term. Further, this research also aimed to reveal the potential underlying mechanisms behind the observed effects of biochar. The specific objectives are listed below:

Objective 1: To determine the long-term effects of biochar on plant production and plant nutrient uptake in boreal conditions in two contrasting soil types with different fertility (**I**)

Objective 2: To assess the long-term effects of biochar on soil physical and hydrological properties (**I**)

Objective 3: To investigate the effects of biochar on the fate of fertilizer ammonium and nitrate, and to evaluate the potential of biochar for effective use of fertilizer N (**II, III, IV**)

Objective 4: To assess the short- and long-term effects of biochar on soil GHG (CO_2, CH_4, and N_2O) emissions and identify the key soil and biochar properties involved (**I, II, IV**)

3 MATERIALS AND METHODS

3.1 EXPERIMENTS AND WEATHER

This research is based on the data from four established field experiments conducted in Finnish agricultural soils, as well as one ^{15}N labeling greenhouse experiment (Table 1 and Table 2). In the field experiments, the biochars were applied in the respective treatments only at the beginning of the experiment. The different field experiments contain several treatments, but only certain treatments were chosen for the selected objectives.

Table 1. General overview of the measurements and analyses of the experiments.

Objective	Experiments	Descriptions of measurements and analyses	Paper
1	- Viikki-1 (Viikki-Stagnosol) - Viikki-2 (Viikki-Umbrisol)	- Estimated plant aboveground biomass from 2010–2018 - Collected plant samples from 2010–2018 - Plant nutrient analysis with ICP-OES	**I**
2	- Viikki-1 - Viikki-2	- Collected undisturbed soil samples after harvest in 2017 - Analyzed soil physical properties: bulk density, porosity, water retention characteristics	**I**
3	- ^{15}N Greenhouse experiment - Qvidja	- Measurement of plant N uptake and N leaching in both greenhouse and Qvidja field experiments - Analyzed soil mineral N content and microbial biomass in Qvidja - ^{15}N analysis in plant biomass, soil, and leachates in the greenhouse experiment	**II, III, IV** **III, IV** **II**
4	- Jokioinen - Qvidja - Viikki-1 - Viikki-2 - ^{15}N Greenhouse experiment	- Gas sampling and analysis with Gas chromatography (GC) over the growing season in 2018 - *In situ* GHG measurement with automated portable FTIR analyzer after sowing and harvesting in 2017 and 2018 in Viikki fields - GHG measurement from greenhouse experiment after ^{15}N fertilizer addition	**IV** **I** **II**

3.1.1 VIIKKI FIELD EXPERIMENTS (I)

There were two long-term biochar field experiments in Viikki with contrasting soil properties (Table 2 and Table 3). One experiment was conducted on a fine-textured fertile Stagnosol (Viikki-1), where biochar was applied in May 2010. This experiment consisted of three identical sub-experiments. Another experiment was conducted on a coarse-textured nutrient-poor Umbrisol (Viikki-2), where biochar was applied in May 2011. Both fields used a split-plot experimental design, each with four replicated blocks. In Viikki-1, the main-plot factor was biochar application rate (levels of 0, 5, and 10 t ha^{-1}); the sub-plot factor was fertilization rate (levels of 30%, 65%, and 100% of recommended fertilization). Similarly, in Viikki-2, the main-plot factor was biochar application rate (levels of 0, 5, 10, 20, and 30 t ha^{-1}); the sub-plot factor was fertilization type [control (no fertilizer application), organic fertilizer (meat bone meal), and mineral (synthetic) fertilizer]. All major Finnish field crops were rotated over the experimental years 2010–2018 (Table 4). In these fields, the required amounts of mineral or organic fertilizers were applied as per the specific crop need recommended by Viljavuuspalvelu Oy (2000), except for the years 2014 and 2015, when no fertilizers were applied to Viikki-2. Only the extreme treatment plots for each experiment (Viikki-1: 0 and 10 t ha^{-1} biochar application rate with 30% and 100% recommended fertilizer; Viikki-2: 0 and 30 t ha^{-1} biochar application rates with all three fertilization levels) were considered (Table 2).

In the Viikki fields, plant aboveground biomass and plant elemental contents were measured from 2010 to 2018. In addition, soil physical properties were measured after harvesting in 2017. The GHG emissions were also measured *in situ* with a portable FTIR analyzer (after sowing and harvesting in growing seasons 2017 and 2018), and with a manual static chamber method throughout the growing season of 2018 (see section 3.3.4). Soil microbial biomass carbon (MBC) and nitrogen (MBN), and soil mineral nitrogen were also periodically measured, along with crop grain yield in the growing season of 2018.

3.1.2 JOKIOINEN FIELD EXPERIMENT (IV)

In Jokioinen, a field experiment was set up in a Stagnosol with a clayey soil texture that was treated with a single biochar application in the autumn of 2016. The experiment consisted of two treatments: (fertilized) control and biochar with five replicates. From Jokioinen (**IV**), only the data from the 2018 growing season was included: the experimental plant was oats fertilized with 90 kg N ha^{-1} and 10 kg P ha^{-1}. GHG emissions, soil MBC, MBN, mineral N, and crop grain yield were measured in growing season of 2018.

Table 2. Details about the experiments and the plots selected for studying the objectives in this dissertation.

Paper	Experiment/Soil type	Established year	Experimental design	Treatments	Selected plots / Remarks
I, IV	Viikki-1 (Fertile Stagnosol, sandy clay loam texture)	2010	Split-plot design with three identically designed sub-experiments (4 replicates)	- Main plot factor: Biochar rate (0, 5, and 10 t ha^{-1}) - Sub plot factor: Fertilization rate (30%, 65% and 100% of recommended fertilization)	i) For objectives 1 and 2: Only extreme treatments with the highest and lowest rates of biochar (0 and 10 t ha^{-1}) and fertilizer (30% and 100%) applied were selected from all three sub-experiments. ii) For objective 4: Plots with 10 t ha^{-1} biochar with 100% fertilizer rate and 100% fertilizer only treatments were chosen from one sub-experiment. *In situ* GHG measurement with FTIR analyzer was carried out from the plots as in (i).
I, IV	Viikki-2 (Nutrient-poor Umbrisol, loamy sand texture)	2011	Split-plot design (4 replicates)	- Main plot factor: Biochar rate (0, 5, 10, 20, and 30 t ha^{-1}) - Sub plot factor: Fertilization type [Control, Organic (Meat bone meal), and Mineral (synthetic) fertilizer]	i) For objectives 1 and 2: Extreme treatments only with the highest and lowest rates of biochar (0 and 30 t ha^{-1}) from all three types of fertilization were selected. ii) For objective 4: Plots with 30 t ha^{-1} biochar with mineral fertilizer and mineral fertilizer only treatments were selected. *In situ* GHG measurement was carried out from the plots as in (i).
III, IV	Qvidja (Cambisol, clayey texture)	2016	Randomized complete block design (RCBD) (3 replicates)	- Unfertilized control - Fertilized control (80 kg N ha^{-1}) - Spruce biochar (20.6 t ha^{-1}) - Willow biochar (33.4 t ha^{-1})	The experiment consisted of organic soil amendment treatments. For this study, only biochar and control treatments were selected. The biochar treatments received the same amount of fertilizers as in the fertilized control.
IV	Jokioinen (Stagnosol, clayey texture)	2016	RCBD (5 replicates)	- Fertilized control - Biochar (30 t ha^{-1})	The biochar treatment received the same amount of fertilizers as in the fertilized control.
II	Greenhouse experiment (Sandy loam texture)	2018	RCBD (5 replicates)	- Control - Fertilizer only - 1% BC1 - 5% BC1 - 1% BC2 - 5% BC2	BC1 and BC2 are RPK Hiili biochar and Kon-Tiki-produced biochar, respectively (Table 5). The biochar treatments and fertilizer-only treatment separately received fertilizers as $^{15}NH_4NO_3$ and $NH_4{}^{15}NO_3$ (equivalent to 100 kg N ha^{-1} in field condition).

Table 3. Initial physico-chemical properties of soils in the experiments.

Experiments	pH	EC ($\mu S\ cm^{-1}$)	Sand (%)	Silt (%)	Clay (%)	Total C (%)	Total N (%)	CEC (cmol (+) kg^{-1})
Jokioinen	5.7	99	15	21	64	5.1	0.4	-
Qvidja	6.4	1500	12	34	54	2.4	0.3	18.2
Viikki-1	6.6	141	50	26	24	3.4	2.9	-
Viikki-2	6.4	76	83	15	2	3.2	2.4	-
Greenhouse experiment	6.9	85	55	35	10	1.1	0.1	-

EC = Electrical conductivity, CEC = Cation exchange capacity

Table 4. Crops grown in the field experiments in different years.

	Viikki-1			Viikki-2	Qvidja	Jokioinen
Year	Sub-experiment 1	Sub-experiment 2	Sub-experiment 3			
2010	Faba bean	Turnip rape	Wheat	-		
2011	Wheat	Faba bean	Turnip rape	Wheat		
2012	Turnip rape	Wheat	Faba bean	Wheat		
2013	Barley	Barley	Barley	Barley		
2014	Grass (Timothy + red clover)	Grass	Grass	Grass		
2015	Grass	Grass	Grass	Grass		
2016	Peas	Barley	Oats	Oats		
2017	Barley	Oats	Peas	Peas	Wheat	
2018	Oats	Peas	Barley	Barley	Oats	Oats

Latin names: Faba bean, (*Vicia faba* L.), Turnip rape (*Brassica rapa* L.), Wheat (*Triticum aestivum* L.), Barley (*Hordeum vulgare* L.), Timothy (*Phleum pretense* L.), Red clover (*Trifolium pratense* L.), Peas (*Pisum sativum* L.), Oats (*Avena sativa* L.).

3.1.3 QVIDJA FIELD EXPERIMENT (III, IV)

The Qvidja field experiment was established in a Cambisol with a clayey soil texture, where biochar was applied in the autumn of 2016. The experiment consisted of organic amendment treatments including biochar treatments, but for this dissertation, only four treatments were included: unfertilized control, fertilized control, spruce biochar, and willow biochar. Wheat and oats were the experimental plants in the growing seasons of 2017 and 2018, respectively. The fertilized treatments received 80 kg N ha^{-1} in both years.

In Qvidja, the field N leaching was measured during the growing season of 2017, the following winter, and the growing season of 2018 using the resin bag method. Moreover, GHG, soil MBC, MBN, mineral N, and crop grain yield were measured in the growing season of 2018.

3.1.4 WEATHER CONDITIONS AT THE SITES OF FIELD EXPERIMENTS

The growing seasons (May to September) of 2011, 2012, 2014, and 2016 received 9–39% more precipitation compared to the long-term average of 1981–2010 (FMI, 2020) in the Viikki fields (**I**). In Qvidja, the amounts of monthly precipitation in May, July, and September of the growing season of 2017 were 53%, 70%, and 43% lower than the long-term average, respectively. Conversely, winter 2017/2018 was wetter than the long-term average, especially the months of October and December 2017, when the monthly precipitation was 38% and 101% higher than the long-term average, respectively (**III**). The growing season in 2018 was extremely dry in all four field experimental sites. The amounts of mean monthly precipitation were consistently lower from May to August compared to the long-term average in all four fields. In 2018, the mean monthly precipitation from May to August was 20–79%, 21–66%, and 17–53% lower than the long-term average in the Viikki, Qvidja, and Jokioinen fields, respectively (**IV**). The extremely dry period after sowing during May and June had hampered the germination of seeds in the growing season of 2018. In Viikki-2, the common flax (*Linum usitatissimum* L.) initially sown on 11 May 2018 in Viikki-2 failed to establish, and the field was resown with barley on 14 June 2018. In Qvidja, to overcome the drought condition, the field was irrigated with 40–50 mm of water during a period of 18 hours on 30 June 2018.

3.1.5 ^{15}N LABELING GREENHOUSE EXPERIMENT (II)

For the ^{15}N labeling greenhouse experiment, pots (6 cm × 6 cm × 6 cm) with holes at the bottom were lined with nylon mesh of 50 µm mesh size to prevent the loss of soil while allowing a free flow of water. The pots were filled with 100 g of soil on a dry weight basis at 50% water holding capacity. Two types of biochars were used in the pot experiment: commercial biochar produced by RPK Hiili Oy (BC1), and Kon-Tiki produced biochar (BC2). Both biochar types were applied at two application rates: 1% and 5%. The treatments consisted of control, fertilizer-only, 1% BC1, 5% BC1, 1% BC2 and 5% BC2, each with five replicates. All the biochar treatments also received N fertilizer as in the fertilizer-only treatment. ^{15}N-enriched fertilizers were applied to all five treatments except the control. Each of the five fertilized treatments contained two groups, receiving fertilizers as either $^{15}NH_4NO3$ or $NH_4{}^{15}NO_3$. The respective types and amounts of biochars were added and mixed properly in the respective treatments. Italian ryegrass (*Lolium* *multiflorum*) seeds were then spread and gently hand-pressed on top of the soil or soil-biochar mixture. These pots were placed inside another bigger pot (9 cm diameter × 6 cm height) for collecting leachate during the leaching test and watering the plants from below. After germination, 2 mL of 2.5 mg N mL^{-1} 10 atom% (at%) $^{15}NH_4NO_3$ or $NH_4{}^{15}NO_3$ solution was pipetted over the pots. The applied N fertilizer corresponded to 100 kg N ha^{-1} application in the field. N leaching tests were periodically carried out four times (days 4, 12, 17, and 24 after the application of ^{15}N labeled fertilizers) during the 33-day long experiment while fluxes of GHG were measured after the addition of fertilizer. At the end of the experiment, above and below-ground plant biomass, as well as N and ^{15}N contents of plant and soil samples were measured to determine the biochar effect on plant N uptake and soil N retention.

3.2 BIOCHARS

All biochars used in this study were prepared from wood, however, the wood species, pyrolysis conditions, application rates, and properties of biochars were different (Table 5). The biochars used were produced at pyrolysis temperature >400°C. The pH of the biochars was highly alkaline (pH 8–10) and contained 75–90% C contents. The application rates ranged from 10–33 t ha^{-1} in the field experiments, and 1% and 5% (w/w) in the greenhouse experiment. The spruce biochar used in Qvidja and Viikki-1, and the biochar produced from the Kon-Tiki kiln had a noticeably higher specific surface area.

Table 5. The feedstock, pyrolysis condition, and general properties of biochars used in this research.

Field	Feedstock	Pyrolysis technique, time/ unit	Pyrolysis temperature (°C)	pH	Carbon content (%)	Specific surface area ($m^2 g^{-1}$)	C:N	Organic matter (%)	Water-soluble N ($mg kg^{-1}$)	Water-soluble P ($mg kg^{-1}$)
Jokioinen	Chipped forest residue	continuous slow pyrolysis (Raussin metalli Ky, Sippola, Finland)	450	8.2	80.0	-	100	-	-	-
Qvidja	Spruce biochar	retort slow pyrolysis (RPK Hilli Oy, Mikkeli, Finland)	450	8.3	89.6	328	221	99.1	<5	3
	Willow biochar	continuous slow pyrolysis (Raussin metalli Ky, Sippola, Finland)	450	9.8	75.3	1.3	48	88.8	14	100
Viikki-1	Chipped spruce and pine	continuous, slow (15 min) (Preseco Oy, Lempäälä, Finland)	500–600	10.8	87.8	34.1	142	-	-	-
Viikki-2	Chipped spruce	continuous, slow (15 min) (Preseco Oy, Lempäälä, Finland)	500–600	8.1	88.2	265	251	-	-	-
Greenhouse experiment	BC1 (Mixed hardwood)	retort slow pyrolysis (RPK Hiili Oy, Mikkeli, Finland)	400	10.0	83.4	8–24 †	60			
	BC2 (Mixed hardwood)	flame curtain pyrolysis with Kon-Tiki kiln	~680–750 *	9.9	85.9	199	266			

† The specific area of BC1 was referenced from Hellstedt et al. (2018). * Pyrolysis temperature was not measured when producing biochar in the Kon-Tiki kiln; it was referenced from Schmidt and Taylor (2014).

3.3 SAMPLING, MEASUREMENTS, AND ANALYSES

3.3.1 PLANT BIOMASS, YIELD, AND NUTRIENT ANALYSES

The plant samples were taken at the full flowering stage by cutting the plants at 2 cm above the soil surface from 3 × 30 cm of sowing row for cereals, 3 × 50 cm for turnip rape, faba bean, and peas, and from a sampling frame of 30 × 30 cm^2 for grasses from Viikki fields (from 2010–2018). The plant samples were oven-dried at 60°C for 72–96 h and weighed to determine the aboveground biomass (AGB) (**I**). After this, the plant samples were ground and analyzed with a VarioMax CN analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) for C and N contents. The ground plant samples were dry-ashed in a muffle furnace at 500°C, extracted with 0.2 M HCl and then filtered through Whatman™ 589/3 filter paper (ashless). The filtrates were analyzed to determine the concentrations of Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, S, Sr, and Zn by ICP-OES (Thermo Fisher iCAP3600 MFC Duo, Thermo Fisher Scientific, Bremen, Germany). The plant uptake of these elements was calculated by multiplying the elemental concentration by AGB.

The AGB (and root biomass in the greenhouse experiment), C and N contents, and plant N uptake from the Qvidja field in 2018 (**IV**) and the greenhouse experiment (**II**) were measured and calculated similarly. In 2018, the crop grain yields were calculated using mass and moisture content of grains harvested from 20 m^2, 0.0314 m^2, and 11.25 m^2 in Jokioinen, Qvidja, and Viikki fields, respectively (**IV**).

3.3.2 SOIL ANALYSES

Four undisturbed soil samples were taken into steel cylinders from a depth of 2.5–7.5 cm of selected plots in the Viikki fields (200 cm^3 and 100 cm^3 steel cylinders were used for Viikki-1 and Viikki-2, respectively) after harvesting in 2017 to determine bulk density, porosity, and the water retention curve (WRC) (**I**). The WRC was determined with the sand-box method for the matric suctions 3 and 6 kPa (pF 1.5 and 1.8), and the pressure plate method for the matric suctions 10, 50, 100, 250, and 1500 kPa (pF 2, 2.7, 3, 3.4 and 4.2) (Dane and Hopmans, 2002). The plant available water content (AWC) was calculated as the difference in soil water content at 6 kPa and 1500 kPa. After determining WRC, the same undisturbed soil samples were dried at 105°C to calculate the bulk density. Total porosity was calculated from the bulk density assuming a particle density of 2.65 g cm^{-3} for soil particles.

Soil sampling from 0–20 cm depth (12 individual samples pooled to form one composite sample; 3 composite samples per plot) was carried out in Qvidja before the experiment in 2016 and after the first growing season in autumn of 2017. The soil samples were analyzed for basic soil physical and chemical properties such as soil pH, electrical conductivity, CEC, total C, total N, and organic matter contents (Table 6).

In the 2018 growing season, soil samples from a depth of 0–10 cm were taken (10 individual soil samples from each plot pooled for a composite sample) three times (approximately once every month) from all four fields to analyze mineral N content and microbial biomass C (MBC) and N (MBN) (**IV**). In Qvidja, three additional soil samplings were carried out: before and after sowing, and after harvesting. The soil NH_4^+ and NO_3^- contents were measured by extracting 5 g of soil with 25 mL of 1 M KCl by shaking in an orbital shaker (30 minutes, 200 rounds per minute), filtered, and analyzed with Lachat QuikChem 8000 (Zellweger Analytics, Milwaukee, Wisconsin, USA). The chloroform fumigation extraction (CFE) method was used for determining soil MBC and MBN contents. For this, 8 g of fresh sieved soil was fumigated with chloroform inside a desiccator for 24 hours in the dark, followed by extraction with 40 mL of 0.05 M K_2SO_4. A parallel control sample without fumigation was also extracted similarly. Then, dissolved organic carbon (DOC) and total nitrogen (TN) contents of the extract were determined using a Shimadzu TOC–V cph/cpn analyzer (Kyoto, Japan). Microbial biomass carbon (MBC) and nitrogen (MBN) were calculated as the difference in DOC and TN contents in chloroform fumigated and control samples, respectively.

3.3.3 MEASUREMENT OF NITROGEN LEACHING

In the greenhouse experiment, about 45–60 mL of reverse osmosis water was poured on top of the soil in the inner pot for the leaching test (**II**). The added water was allowed to leach through the soil for about 30 minutes, before being collected in the outer pot. The volume of the leachate collected was measured and the concentrations of NH_4^+ and NO_3^- were measured with an automated colorimetric method using Gallery™ Plus Discrete Analyzer (Thermo Scientific™, Vantaa, Finland). The ^{15}N in the leachate was measured after concentrating the leached NH_4^+ and NO_3^- in acidified filter paper (Sørensen and Jensen, 1991) using an elemental analysis (CE 1110, Thermo Electron, Milan, Italy) coupled in continuous flow mode to a Finnigan MAT Delta PLUS Isotope Ratio Mass Spectrometer (IRMS, Thermo Scientific, Bremen, Germany).

In the resin bag method (used in **III, IV**), the water-permeable bags containing ion-exchange resins were placed under the plough layer (approximately 20 cm deep) after coring the soil using a PVC tube (10 cm diameter). The cored soil was placed on top of the resin bag. The NH_4^+ and NO_3^- accumulated in the resins were used as a measure of mineral N leached over the period that the resin bag remained in the field. During each growing season in 2017 and 2018, the resin bags were replaced approximately once a month (three times) between sowing and harvesting. After harvesting in 2017, the resin bags were removed only in spring 2018, before the start of the growing season. After removing the resin bag from the soil, it was cleaned with Milli-Q water before extracting twice with 100 mL of 1 M NaCl (shaken in an orbital shaker for 30 minutes at 169 rounds per minute). The extracts were filtered and analyzed at 660 nm (NH_4^+) and 540 nm (NO_3^-) wavelengths using a microplate spectrophotometer (µQuant, BioTek Instruments, Bad Friedrichshall, Germany). The cumulative NH_4^+ or NO_3^- leaching for each growing season was calculated by adding the amounts of NH_4^+ or NO_3^- leached in the three measurement times.

3.3.4 MEASUREMENT OF GREENHOUSE GASES

The fluxes of GHG (CO_2, CH_4, and N_2O) were measured *in situ* from the Viikki fields (**I**) after sowing and harvesting in the growing seasons of 2017 and 2018 using an automated Fourier Transform Infrared Trace Gas Analyzer (FTIR-TGA) (Gasmet DX4015, Gasmet, Helsinki, Finland).

In the greenhouse experiment, the fluxes of GHG were measured after adding N fertilizer. For measuring the GHG fluxes, each pot was placed in a glass jar (3.1 L volume) with an air-tight nozzle fixed in its lid for gas sampling (**II**). After over-pressurizing the glass jar with 80 mL of ambient air, 20 mL of gas samples were taken into 12 mL helium (He) flushed evacuated Exetainers® (Labco Scientific, High Wycombe, UK) at 0, 4, 20, and 24 h after closing the jars. The concentrations of GHG (CO_2, CH_4, and N_2O) in the gas samples were measured using a gas chromatograph (7890A, Agilent Technologies, California, USA) equipped with a flame ionization detector (FID) and a methanizer for CO_2 and CH_4, and an electron capture detector (ECD) for N_2O.

In the growing season of 2018, the fluxes of GHG were measured from all four field experiments approximately once every two weeks throughout the growing season (**IV**). Each selected plot was installed with a collar of 60 cm × 60 cm in dimension. To measure the GHG fluxes, an opaque aluminum chamber (60 cm × 60 cm × 75 cm) was air-tightly inserted on top of the collar. Then a 20 mL gas sample was withdrawn with a syringe after 0, 10, 20, 30, and 40 minutes and injected into a 12 mL evacuated vial (Exetainer®, Labco Ltd.). The gas samples were analyzed for CO_2, CH_4, and N_2O concentrations using the gas chromatograph similarly as in the greenhouse experiment. The cumulative emissions of each GHG were calculated using linear interpolation between sampling times.

Table 6. Measurements and methods used in the experiments

	Variables	Methods	Reference (Paper)
Biochar	pH	1:2.5 or 1:5 biochar:water (w/v)	**(I-IV)**
	Electrical conductivity	1:2.5 or 1:5 biochar:water (w/v)	**(I-IV)**
	Specific surface area	N_2 adsorption	**(I-IV)**
	Ash content	Gravimetric method (ashed at 500°C for 3 hours)	**(I-IV)**
	Total C and N	Dry combustion	**(I-IV)**
Soil	pH	1:5 soil:water (w/v)	Vuorinen and Mäkitie (1955) **(III)**
	Electrical conductivity	1:5 soil:water (w/v)	Vuorinen and Mäkitie (1955) **(III)**
	CEC	Barium chloride method	ISO 11260:1994
	Organic matter content	Loss on ignition	Nelson and Sommers (1983) **(III)**
	Total C and N	Dry combustion	**(III)**
	Water retention curve	Sandbox at pF 1.5 and 1.8, pressure plate at pF 2, 2.7, 3, 3.4 and 4.2	Dane and Hopmans (2002) **(I)**
	NH_4^+ and NO_3^- contents	1M KCl extraction and analysis with an automated flow injection analyzer (Lachat analyzer)	**(III, IV)**
	^{15}N content	Analysis with Isotope Ratio Mass Spectrometer (IRMS)	**(II)**
	MBC and MBN	Chloroform fumigation extraction	Vance et al. (1987) **(III, IV)**
Plants	Biomass (aboveground and root)	Oven-drying at 60°C for 48–96 hours	**(I, II, IV)**
	Elemental contents	Dry-ashing at 500°C for 2 hours, extraction with 0.2 M HCl and analysis with ICP-OES	Miller (1998) **(I)**
	C and N contents	Dry combustion	**(I, IV)**
	^{15}N content	Analysis with IRMS	**(II)**
Leachates	NH_4^+ and NO_3^- contents	Analysis of filtrates with a discrete analyzer	**(II)**
	$^{15}NH_4^+$ and $^{15}NO_3^-$ contents	Sequential diffusion of leached NH_4^+ and NO_3^- in acidified filter paper and analysis with IRMS	Sørensen and Jensen (1991) **(II)**
	NH_4^+ and NO_3^- contents	Resin bag method, extraction with 1M NaCl and analysis with a spectrophotometer	Hood-Nowotny et al. (2010) **(III, IV)**
Gases	CO_2, CH_4, N_2O	Static chamber method and analysis with an automated portable FTIR analyzer	**(I)**
	CO_2, CH_4, N_2O	Air sampling from the gas-tight incubation jar and analysis with a gas chromatograph	**(II)**
	CO_2, CH_4, N_2O	Static chamber method and analysis with a gas chromatograph	**(IV)**

3.4 CALCULATION AND STATISTICAL ANALYSIS

For Viikki field experiments (2010–2018), the values of above-ground biomass and nutrient contents of plants were normalized to neutralize the variation due to different crops and environmental conditions in different years and sub-experiments (**I**). For normalization, the corresponding individual values of the biochar treatment plots with 100% mineral fertilizer level were divided by the average of the control with the same fertilization but without biochar for each year. Then, linear regression analysis was carried out between the normalized values *vs*. year.

For the greenhouse experiment (**II**), the N derived from fertilizer (Ndff) and N derived from soil (Nds) in plant biomass, soil, and leachate were calculated using Eqs. 1, 2, 3 and 4 (Table 7). The N use efficiency (NUE) was calculated from Qvidja 2018 growing season data (Eq. 5) (**IV**). The yield-normalized summed emissions of CH_4 and N_2O were calculated from all four field experiments in the 2018 growing season (Eqs. 6, 7) (**IV**). In addition, for each field, the relative difference in the emissions of CO_2 (ΔCO_2), CH_4 (ΔCH_4), and N_2O (ΔN_2O) were also calculated (Eq. 8). The relationship between ΔCO_2 or ΔN_2O or ΔCH_4 and soil properties (such as sand, silt, clay, and initial soil C contents) and biochar properties (such as biochar pH, biochar C content, and C:N) were analyzed using Pearson correlation analysis and redundancy analysis.

The statistical analyses were carried out in the R environment. The data were checked for normality (Shapiro-Wilk test or Q-Q plot) and homogeneity of variances (Levene's test or residuals *vs*. fitted plot). The statistical significance was tested with either linear mixed-effects model (**I, IV**) or analysis of variance (ANOVA; **II, III**). When the effects of biochar, and fertilizer were considered (**I**), biochar, fertilizer, and their interactions were used as fixed factors, while replicated block and their interactions were used as random factors in the linear mixed-effects model. When only the effect of biochar was considered (**IV**), biochar treatment (and measurement time) was considered as the fixed factor and replicated block as the random factor. When linear mixed-effects models were carried out, post hoc tests were computed using the "emmeans" function (emmeans package) with the Tukey method for p-value adjustments and a significance level of $p<0.05$ specified in the "cld" function (multcompView package). When ANOVA was used, Tukey HSD (**II**) or Dunnett's two-sided t-test (**III**) were carried out.

Table 7. Table of equations.

Equations		Reference (Paper)
$Ndf_{^{15}NH_4^+} = \frac{T(A_s - A_b)}{A_f}$	Eq. (1)	Powlson and Barraclough (1993) (**II**)
$Ndf_{^{15}NO_3^-} = \frac{T(A_s - A_b)}{A_f}$	Eq. (2)	Powlson and Barraclough (1993) (**II**)
$Ndff = Ndf_{^{15}NH_4^+} + Ndf_{^{15}NO_3^-}$	Eq. (3)	Powlson and Barraclough (1993) (**II**)
$Nds = T - Ndff$	Eq. (4)	Powlson and Barraclough (1993) (**II**)
$NUE = \frac{NU_T - NU_C}{N_F} \times 100\%$	Eq. (5)	Liao et al. (2020) (**IV**)
$CO_2 - eq. = 25 \times E_{CH_4} + 298 \times E_{N_2O}$	Eq. (6)	Yang et al. (2020b) (**IV**)
$GHGI = \frac{CO_2 - eq.}{Y}$	Eq. (7)	Yang et al. (2020b) (**IV**)
$\Delta CO_2 / \Delta CH_4 / \Delta N_2O = \frac{E_{BC} - E_{FC}}{\lvert E_{FC} \rvert} \times 100\%$	Eq. (8)	(**IV**)

Descriptions of the terms used in the equations are as follows:

T	=	total N content in samples (plant/soil/leachate; mg N pot^{-1}/µg N pot^{-1})
A_s	=	at% ^{15}N excess of the sample (plant/soil/leachate)
A_b	=	at% ^{15}N excess of the control (without receiving ^{15}N fertilizer)
A_f	=	at% ^{15}N excess of $^{15}NH_4NO_3$ or $NH_4{}^{15}NO_3$
$Ndf_{^{15}NH_4^+}$	=	N derived from $^{15}NH_4NO_3$ (mg ^{15}N pot^{-1} or µg ^{15}N pot^{-1})
$Ndf_{^{15}NO_3^-}$	=	N derived from $NH_4{}^{15}NO_3$ (mg ^{15}N pot^{-1} or µg ^{15}N pot^{-1})
Nds	=	N derived from soil (+ biochar) mixture (mg ^{15}N pot^{-1} or µg ^{15}N pot^{-1})
NUE	=	nitrogen use efficiency (%)
NU_T	=	N uptake in a treated plot (kg N ha^{-1})
NU_C	=	average of N uptake in the unfertilized control plot (kg N ha^{-1})
N_F	=	amount of N fertilizer applied (kg N ha^{-1})
CO_2–eq.	=	CO_2 equivalent of cumulative CH_4 + N_2O (kg CO_2-e ha^{-1})
Y	=	dry grain yield of crop (t ha^{-1})
GHGI	=	yield-normalized sum of CH_4 and N_2O emissions (greenhouse gas intensity; kg CO_2-e t^{-1} grain yield)
E_{CH_4}	=	total cumulative emissions of CH_4 (kg CH_4 ha^{-1})
E_{N_2O}	=	total cumulative emissions of N_2O (kg N_2O ha^{-1})
E_{BC}	=	cumulative emissions of CO_2 or CH_4 or N_2O in the biochar treatments (kg CO_2-C ha^{-1} or kg CH_4-C ha^{-1} or kg N_2O-N ha^{-1})
E_{FC}	=	average cumulative emissions of CO_2 or CH_4 or N_2O in the (fertilized) control treatment (kg C ha^{-1} or kg N ha^{-1})

4 RESULTS AND DISCUSSION

4.1 LONG-TERM EFFECTS OF ADDED BIOCHAR ON PLANT GROWTH AND NUTRIENT UPTAKE (I)

The softwood biochars had limited effects on plant AGB and plant nutrient uptake. Only the noticeable effects of biochars observed are presented and discussed here. The biochars increased plant AGB yield only in two cases during eight years of the field experiments in Viikki-1 and Viikki-2 (**I**). This positive effect of the biochar was observed only in Viikki-1 in the growing seasons of 2013 (3 years after biochar addition) and 2016 (6 years after biochar addition), when the fields were cropped with barley and peas, respectively (Figure 3). In both cases, biochar increased AGB at 100% recommended fertilization rate plots, but no effects of biochar were observed at the 30% fertilization rate plots. This positive effect of biochar is most likely related to the pre-crop effect because in both cases, the fields were cropped with legumes – capable of symbiotic N_2-fixation – in the previous growing season (i.e. faba bean before barley in 2012, and red clover before peas in 2014–2015). These N_2-fixing plants could increase the availability of N to the plants in the following growing season (Bruulsema and Christie, 1987; Peoples et al., 2009). Consequently, in these two exceptional cases, plant N uptake increased in the biochar treatment at the 100% fertilizer application rate along with the increased plant uptake of other macronutrients, such as P, K, Ca, Mg, and S (Table 8).

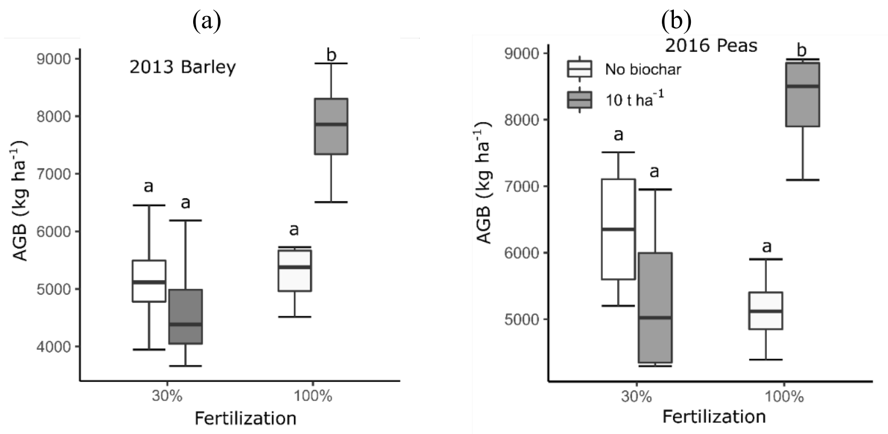

Figure 3. Aboveground biomass (AGB) at the experimental treatments (30% or 100% of recommended fertilization level, each with or without added 10 t ha^{-1} biochar) in (a) 2013 (sub-experiment 2) and (b) 2016 (sub-experiment 1), when biochar-fertilization interaction was found to be statistically significant (**I**).

Table 8. Uptake of plant nutrients in peas in 2016 (sub-experiment 1) and barley in 2013 (sub-experiment 2) in the experimental treatments in Viikki-1 (**I**), when exceptional biochar-fertilizer interaction effects were observed.

Year/ Crop	Fertili-zation	Biochar (t ha^{-1})	N (mg kg^{-1})	P (mg kg^{-1})	K (mg kg^{-1})	Ca (mg kg^{-1})	Mg (mg kg^{-1})	S (mg kg^{-1})
2016	30%	0	121.9 ab	13.73 a	64.9 a	61.02 a	13.32 a	11.12 a
Peas		10	94.5 a	10.74 a	50.2 a	51.54 a	11.04 a	8.78 a
	100%	0	92.1 a	11.16 a	59.4 a	46.36 a	10.49 a	13.06 a
		10	193.8 b	25.70 b	165.7 b	91.06 b	20.65 b	22.57 b
	p-value		**0.003**	**< 0.001**	**0.001**	**< 0.001**	**< 0.001**	**< 0.001**
2013	30%	0	76.6 a	13.40 a	47.9 a	10.25 ab	5.66 a	3.38 ab
Barley		10	59.9 a	11.56 a	34.9 a	8.17 a	5.36 a	2.81 a
	100%	0	80.9 ab	12.71 a	46.7 a	10.08 ab	5.09 a	3.34 ab
		10	113.1 b	19.21 b	77.3 b	14.44 b	8.81 b	4.68 b
	p-value		**0.014**	**0.005**	**0.007**	**0.007**	**0.001**	**0.022**

Different letters indicate significant differences across treatments.

Most noticeably, the spruce biochar increased plant K content in five out of eight growing seasons in Viikki-2 ($p<0.1$) (**I**), which is in agreement with other studies (Gaskin et al., 2010; Biederman and Harpole, 2013; Oram et al., 2014). The increase in plant content and uptake of K in 2014 and 2015 (when no fertilizers were applied) suggests that K present in biochars can enhance plant K availability for a longer period. This long-term effect of biochar on plant K availability could also be due to reduction in loss of fertilizer K by biochar through leaching (Kuo et al., 2020), or conversion of the unavailable K in biochar and soil clay minerals to the plant available form (Wang et al., 2018; Zhang et al., 2020b).

The biochar distinctly reduced plant Al and Na contents in Viikki-1 (**I**). Accordingly, the effectiveness of biochars in reducing plant Na content and uptake from saline soils has been reported previously (Akhtar et al., 2015; Hammer et al., 2015; Feng et al., 2018). Such reduction in plant availability of Na could be due to the antagonistic effect of K (Glaser et al., 2015). Biochar reduced the plant Al contents mostly in the initial years (2010-2012) after application in Viikki-1. The reduction in Al availability could be due to increased soil pH after biochar addition (Hale et al., 2020) or electrostatic surface adsorption on biochar surface, or complexation of Al with hydroxyl and carboxyl groups on the biochar surface (Qian and Chen, 2013). Since the biochar had a small liming effect and no effect on soil pH right after application (Tammeorg et al., 2014a), the adsorption or complexation of Al on the biochar surface seems a plausible mechanism behind the reduced plant Al availability.

The linear regression analysis of year *vs*. normalized values (the ratio of AGB or plant elemental contents of biochar and non-biochar treatments; see section 3.4) showed that, with time, biochar tended to increase plant availability of P, K, Mg, S, Al, Cu, Fe, and Ni in Viikki-1, and Cd and Ni in Viikki-2 ($p<0.1$; **I**). Among these nutrients, the most distinct increase was observed for Cu in Viikki-1 ($R^2 = 0.16$; $p<0.001$) and Ni in Viikki-2 ($R^2 = 0.35$; $p<0.001$). The increased plant availability of nutrients as biochars age in the fields could be due to

i) an increase in the ability of the biochar to withhold nutrients (applied as fertilizers or present in soils) as they age in the fields because of surface oxidation (Cheng et al., 2006; Mia et al., 2017) or the formation of organic coatings (Hagemann et al., 2017a),

ii) release of the nutrients present in the biochar because of biochar dissolution due to weathering (Spokas et al., 2014),

iii) release of initially sorbed elements on the biochar surface to the soil due to weathering (Zhong et al., 2020). The plant Al contents over the years in Viikki-1 supports that biochar decreased plant availability of soil Al right after application, consequently decreasing plant Al contents in the initial years (2010–2012). With time, the normalized value of Al increased, and the differences in plant Al contents between biochar and non-biochar treatments became insignificant suggesting that initially immobilized Al by biochars might have become available for plant uptake.

On the other hand, the normalized value of Mn decreased over time in Viikki-2 ($R^2 = 0.15$; $p = 0.03$; **I**). This signifies biochar acted as a source of plant-available Mn or increased solubility of Mn in the soil at the beginning, which faded over the years.

4.2 LONG-TERM EFFECTS OF BIOCHAR ON SOIL PHYSICAL AND HYDROLOGICAL PROPERTIES (I)

No long-term effects of the softwood biochars on bulk density, porosity, or water retention characteristics of the topsoils were observed in either Viikki-1 or Viikki-2 (**I**). In the initial years after the biochar application, some positive effects were observed, such as reduced bulk density, increased soil porosity, and increased plant available water content, especially in the coarse-textured soil of Viikki-2 (Tammeorg et al., 2014b). However, after seven growing seasons, those effects faded out, which points towards the loss of biochar particles from topsoil over the years. The loss could be due to physical breakdown of biochar particles followed by mineralization (de la Rosa et al., 2018) and dissolution/leaching of biochar particles (Spokas et al., 2014). In addition, the biochar particles might have also moved down the soil profile (Kätterer et al., 2019). It was previously found in the initial years (2010–2012) that the recovery of SOC in the topsoil was higher in Viikki-1 with fine-textured soil than in Viikki-2 with coarse-textured soil (Tammeorg et al., 2014a; Tammeorg et al., 2014b), indicating that the downward movement of biochar in the soil profile is a more plausible explanation for the loss of biochar from the topsoil. Moreover, wind/water erosion might also lead to the loss of biochar particles. Similarly, the filling of biochar pores with clay and soil organic matter also reduces the water holding capacity of biochar amended soil in the long run (Wang et al., 2019).

4.3 EFFECTS OF BIOCHAR ON NITROGEN DYNAMICS (II, III, IV)

4.3.1 EFFECTS OF BIOCHAR ON NITROGEN RETENTION AND NITROGEN USE EFFICIENCY

In both the greenhouse experiment (**II**) and the Qvidja field experiment (**III**, **IV**), biochars increased plant N uptake (Figure 4) and reduced N leaching (Figure 5). These effects were most prominent in the 5% biochar application rate treatments in the greenhouse experiment (**II**) and in the spruce biochar treatment in the Qvidja field experiment (**IV**). The spruce biochar treatments also increased the retention of NO_3^- in soil (**III**, **IV**). In both greenhouse and field experiments, all biochars tended to reduce N_2O emissions (see section 4.4). These results suggest that biochars can retain highly mobile NO_3^- ions in soils, preventing them from leaching, decreasing their gaseous losses while keeping them available for plant uptake, ultimately increasing nitrogen use efficiency (**IV**). However, compared to the fertilized control treatment, the differences in soil NO_3^- retention, plant N uptake, and NUE were clearly greater in the spruce biochar than the willow biochar treatments, which could be because of the significantly greater specific surface area of the spruce biochar (**IV**).

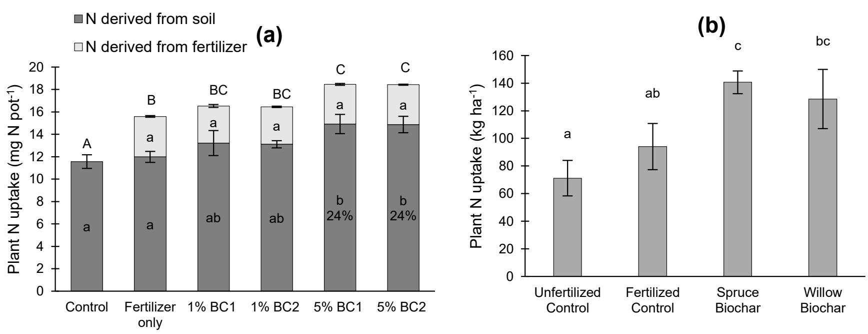

Figure 4. Plant N uptake at the experimental treatments in the (a) greenhouse experiment (**II**) and (b) Qvidja field experiment in the growing season of 2018 (**IV**). Different letters across the treatment refer to the statistical differences between them (p<0.05).

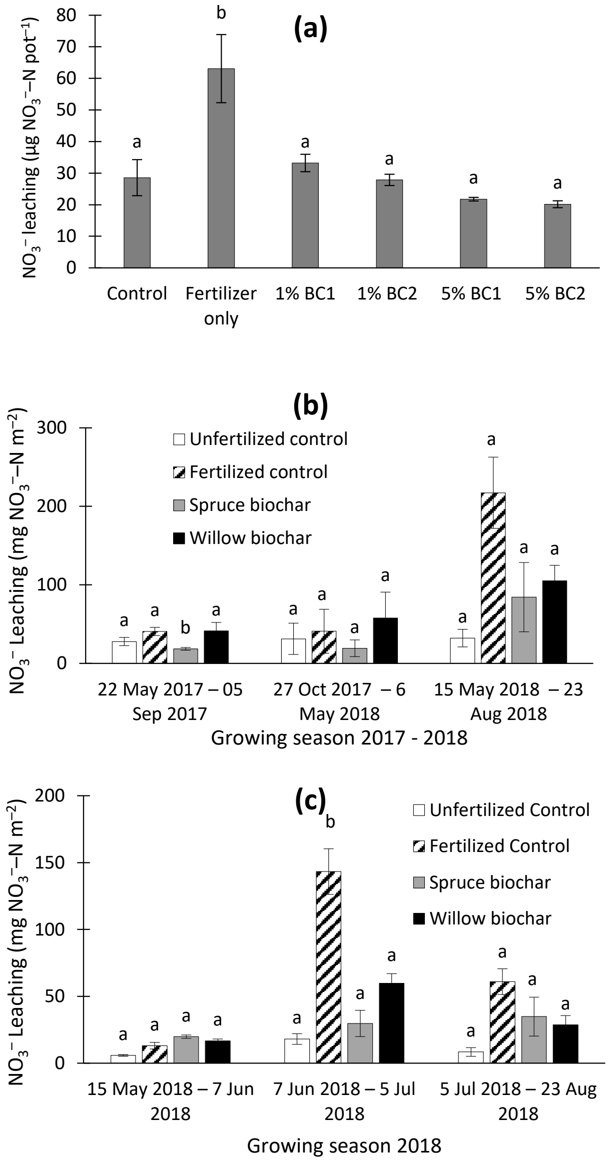

Figure 5. Nitrate leaching in the experimental treatments of the greenhouse and Qvidja field experiments. a) Cumulative NO_3^-–N leaching in the greenhouse experiment. b) Cumulative NO_3^-–N leaching from the cropped soil during the growing season of 2017 (22 May 2017 – 5 Sep 2017), from the uncropped soil during winter 2017/2018 (27 Oct 2017 – 6 May 2018), and from cropped soil during the growing season of 2018 (15 May 2018 – 23 Aug 2018) in the Qvidja field experiment. c) NO_3^-–N leaching from cropped soil during three different measurement periods during the growing season of 2018 in the Qvidja field experiment.

Most of the N leaching occurred in the form of NO_3^-. In the greenhouse experiment, both biochar treatments significantly reduced NO_3^- leaching (Figure 5a, **II**). However, in the Qvidja field experiment, the significant reduction in cumulative NO_3^- leaching by the spruce biochar was observed only during the growing season of 2017. No significant differences were observed during winter 2017/2018 or the growing season of 2018, although there was a consistent trend of reduced NO_3^- leaching in the spruce biochar treatment compared to the fertilized control (Figure 5b, **III, IV**). The ability of the biochars to reduce NO_3^- leaching was higher during times when higher NO_3^- leaching could be expected, for instance right after fertilization and during high rainfall events. In the greenhouse experiment, the reduction in NO_3^- leaching by biochars was observed mostly 2 to 4 days after N fertilization (**II**). In the Qvidja field experiment, because of the extremely dry weather – especially at the beginning of the growing season in 2018, NO_3^- leaching was relatively low across all the treatments during the first measurement period (Figure 5c), and hence no effects of the biochars were observed then. However, during the second measurement period, the field was irrigated to meet the plant water demand, and also the first major rainfall events of the growing season had occurred. Consequently, NO_3^- leaching increased in the fertilized control treatment, while NO_3^- leaching in both biochar treatments was significantly reduced. A similar trend was observed during the third measurement period, but most of the leachable NO_3^- might have already been leached or taken up by plants, so no significant differences between the treatments were observed (**IV**).

The increased retention in soil, and thus decreased leaching of NO_3^- by both biochars in the greenhouse experiment (**II**) and by the spruce biochar in the Qvidja field experiment (**IV**) indicate the ability of those biochars for NO_3^- retention. Thus, retained NO_3^- could be strongly held in or on a biochar porous matrix, thereby reducing NO_3^- leaching, although it might not be fully accessible to the plants (Haider et al., 2016; Haider et al., 2017). However, in both the greenhouse experiment and Qvidja field experiment in 2018, the biochars increased plant N uptake and plant growth (**II, IV**), indicating that the captured NO_3^- was slowly released for plant uptake as suggested by Hagemann et al. (2017b). The formation of organic coatings due to the interaction of rich organics and biochars, adding an extra layer of porosity on the surface, has been shown as a mechanism behind the exceptional NO_3^- retention in co-composted biochars (Kammann et al., 2015; Hagemann et al., 2017a; Joseph et al., 2018). Similar modification in surfaces of the spruce biochar could be expected after about one to two years of application due to its continuous interaction with soil, SOC, root exudates, and microbes that might have enhanced its ability to retain and slow release of NO_3^- (Hagemann et al., 2017a). However, the lack of any effect with the willow biochar on NO_3^- leaching (in the growing season of 2017) and soil NO_3^- retention indicates that not all biochars have a tendency for NO_3^- retention.

The contrasting effects between the spruce and willow biochars on NO_3^- retention could be because of their initial surface properties, as the specific surface area of the spruce biochar (328 m^2 g^{-1}) was much greater than that of the willow biochar (1.3 m^2 g^{-1}) (Table 5). The large surface area indicates the presence of many smaller pores (Leng et al., 2021), where the movement of water and dissolved nitrate and other nutrients are confined (Conte et al., 2014). In the growing season of 2018, however, the willow biochar showed a tendency to reduce NO_3^- leaching similar to that of the spruce biochar (Figure 5c). This points towards the possibility of the modification of willow biochar surface by field-aging that helped to increase NO_3^- retention. Alternatively, it could also be because of improved water holding capacity of soil that results from modification of soil structures during extremely dry conditions (Yoo et al., 2014).

4.3.2 EFFECTS OF BIOCHAR ON NH_4^+ VOLATILIZATION

Tracing of ^{15}N isotopes in the greenhouse study (**II**) revealed that the biochar treatments increased the recovery of ^{15}N from the $^{15}NO_3^-$ fertilizer in plants, and decreased that from the $^{15}NH_4^+$ fertilizer. A similar trend was observed in the case of ^{15}N recovery in soils. In both $^{15}NH_4^+$ and $^{15}NO_3^-$ fertilizer treatments, there was a noticeable reduction of $^{15}NH_4^+$ and $^{15}NO_3^-$ leaching in the biochar treatments, although the differences were not always statistically significant. In addition, the biochars significantly reduced N_2O emissions. These findings indicate that when fertilizer was added in the form of NH_4^+, biochars increased the loss of the added N from the plant-soil system. Notably, this loss was not through leaching and N_2O emission, but rather mostly through the volatilization of added $^{15}NH_4^+$ to $^{15}NH_3$. This is also supported by the increase in soil pH after the addition of biochars (**II**). Similar to this result, other studies have also demonstrated that an increase in soil pH after biochar addition enhanced the significant loss of added fertilizer N due to ammonia volatilization (Schomberg et al., 2012; Liu et al., 2018; Dong et al., 2019). However, there are also studies reporting decreased ammonia volatilization after the application of biochars (Mandal et al., 2019; Sun et al., 2019). The pH of soils and biochars are determining factors that impact ammonia volatilization. In a meta-analysis, Sha et al. (2019) observed that ammonia volatilization increased with the addition of high pH biochars (pH >9) or when biochars were combined with ammonia-based fertilizers. They also found that ammonia volatilization increased when biochars are applied in acidic soils (pH <6), probably due to the application of high amounts of high pH biochars.

4.3.3 EFFECTS OF BIOCHAR ON PLANT AVAILABILITY OF SOIL ORGANIC NITROGEN

The increased plant uptake of $^{15}NO_3^-$ fertilizer was offset by the loss of $^{15}NH_4^+$ fertilizer. As a result, the total plant uptake of N derived from NH_4NO_3 fertilizer as a whole was unaffected by the addition of biochars (Figure 4a, **II**). Instead, the increased plant uptake of N in the biochar treatments was derived from sources other than fertilizer, potentially biochar and soil. Usually, N contained in biochars is expected not to be available for plant uptake because of its recalcitrance to microbial decomposition (Clough et al., 2013; Jeffery et al., 2017b; Torres-Rojas et al., 2020; Weng et al., 2020). Therefore, it is likely that the increased plant N uptake was derived from the soil. Biochars have enhanced the mineralization of soil organic N (positive priming effect) and its conversion into the plant available form in other studies as well (Nelissen et al., 2012; Fiorentino et al., 2019). Moreover, the soil used in the greenhouse experiment had been applied with pig slurry manure. Therefore, the soil can be suspected to contain a high amount of labile organic N, which might be easily mineralized by biochars, resulting in high plant N uptake derived from the soil N pool. Since, this soil N pool also includes the N derived from seeds, the effect of biochar on seed germination might have played role in the increased plant N uptake derived from the soil N pool, considering the high seeding rate (about 250 seeds per 100 g soil in a pot with 6×6 cm^2 surface soil area) used in the greenhouse experiment (**II**). Biochars could have promoted the seed germination rate (Solaiman et al., 2012; Das et al., 2020), which is also reflected by the increased plant biomass, especially in the 5% biochar treatments (**II**). As a result, the total amount of N translocated from the total number of germinated seeds to the plant biomass per pot is naturally higher in the biochar treatments. Furthermore, it is likely that a large number of seeds failed to germinate, and hence is possible that the biochars increased the decomposition or mineralization of those ungerminated seeds, releasing their N to be accessible for the growing plants.

4.4 EFFECTS OF BIOCHAR ON GHG EMISSIONS AND GHGI (II, IV)

4.4.1 GHG EMISSIONS

The effects of biochars on N_2O emission varied among the experiments and measurement techniques. Right after fertilization, biochars reduced N_2O emissions by 57–81% in the greenhouse experiment (**II**). Similarly, *in situ* measurement with the FTIR analyzer showed that biochar clearly reduced N_2O emissions only during one measurement following sowing in 2018 in Viikki-2 (**I**). The N_2O fluxes measured by the FTIR analyzer were found to be generally low after harvesting. Biochar had a few significant but inconsistent effects on them depending on fertilization type and year (**I**). Since these measurements were carried out only a few times after sowing and harvesting (in 2017 and 2018 in Viikki fields), the peak emission periods might have been missed. The more intensive GHG measurement campaign on the four fields during the growing season in 2018 using a manual gas sampling technique showed that biochar tended to increase the CO_2 flux in Qvidja and Viikki-2 (**IV**). In Qvidja, a noticeable decrease in N_2O flux was observed in the biochar treatments, especially at the end of the growing season (**IV**).

The increase in CO_2 flux by biochar could be because of increased soil microbial activity, as suggested by the significant correlation between MBN and CO_2 emissions (**IV**). Usually, labile C present in biochars is easily available for microbial consumption. Hence, right after biochar application, higher microbial growth and thus higher CO_2 emissions can be expected (Smith et al., 2010; Luo et al., 2011; Zimmerman et al., 2011; Bruun et al., 2012; Singh and Cowie, 2014). However, the biochars were applied two and seven years before the measurement in Qvidja and Viikki-2 fields, respectively. Thus, the labile C content must have been already depleted by then. It can be suspected that the biochars might have created favorable habitats for microbes by modifying soil structure in the long-term (Hardy et al., 2019). Apart from this, the biochar treatments had higher plant growth in both Qvidja and Viikki-2 (**IV**). The manual measurement technique also included plants inside the chamber (**IV**), therefore the increased aboveground plant and root growth (Xiang et al., 2017; Liu et al., 2021) leading to overall plant respiration also contributed to the higher CO_2 flux at the biochar treatments in these fields.

Although the effects of biochars on N_2O flux were not consistent, the results support the view that biochars suppress N_2O flux, especially during peak emission points (Hüppi et al., 2016). Similar to N leaching, the peak N_2O emissions usually occur right after fertilization (Weitz et al., 2001; Harter et al., 2014) and after a rapid increase in soil moisture as a result of irrigation or high rainfall event (Trost et al., 2013; Barrat et al., 2021). Notably, there was almost no rain for about a month after sowing/fertilizer application in Qvidja in 2018. Therefore, the fertilizer granules applied were not completely dissolved, which led to very little N_2O flux at the beginning of the growing season. However, the later growing season was comparatively wetter and accompanied by a sharp increase in N_2O flux in the fertilized control treatment. Both the spruce and willow biochars suppressed the N_2O flux then. However, due to the large variances, the differences were not statistically significant (Hüppi et al., 2015; Kammann et al., 2017). Such reduction in N_2O flux might be due to an increase in soil pH by the addition of biochars, as observed in the greenhouse study (**II**) and a parallel incubation study using the soil from Qvidja in 2018 (Peltokangas et al., unpublished). In autumn 2017, soil pH tended to increase by 0.1 and 0.5 units in the spruce and willow biochar treatments, respectively, compared to the fertilized control (**III**). Thus, increased soil pH after biochar addition could facilitate the synthesis of N_2O reductase, enhance N_2O reductase genes (nosZ) or increase N_2O reducing microbes that help in the reduction of N_2O to N_2 (Cayuela et al., 2013; Harter et al., 2014; Van Zwieten et al., 2014; Dannenmann et al., 2018; Liao et al., 2021a).

During the denitrification process, NO_3^- is the substrate for the production of N_2O and/or N_2. Therefore, higher NO_3^- content in soil usually results in greater production of N_2O. However, in this research, it was found that even though the spruce biochar increased NO_3^- content in the soil, the biochar either had no effect or tended to decrease N_2O emissions. This supports the concept that the NO_3^- retained in (field-aged) biochar particles may not be accessible to the (denitrifying) microbes (Van Zwieten et al., 2014; Haider et al., 2016; Kammann et al., 2017).

No effects of biochar on CH_4 flux were observed in the greenhouse experiment (**II**) or the field experiments by the manual measurements (**IV**). However, according to the *in situ* measurements with the FTIR analyzer, biochar reduced soil CH_4 uptake in the mineral fertilizer treatment in Viikki-2 in one measurement after sowing in 2018 (**I**). It should be noted that the measurement with FTIR-based analyzers (Gasmet) might not be accurate for such small CH_4 fluxes as observed in this study, because of interference with volatile organic compounds (VOC) (Kohl et al., 2019). Measurement with such automated portable FTIR analyzers is convenient and economical, but the quality of data obtained with such analyzers needs to be verified by comparing with other (manual) measurement techniques.

4.4.2 YIELD-SCALED NON-CO_2 GHG EMISSIONS (GHGI)

The biochars were found to have long-term effects on reducing yield-scaled emissions of CH_4 and N_2O. The biochar significantly reduced yield-scaled emissions of non-CO_2 GHG by 43% in Viikki-2 ($p<0.05$). Similarly, the average yield-scaled emissions were reduced by 64% and 86% by the spruce and willow biochars in Qvidja, respectively, but without statistical significance (**IV**). The reduction in Viikki-2 was mostly because of increased crop yield (statistically significant; $p<0.05$) than decreased emissions of CH_4 or N_2O, whereas in Qvidja, the reduction was contributed by increased crop yield (statistically significant in the spruce biochar treatment; $p<0.05$) as well as decreased N_2O emissions. The increased crop yield in these fields could be attributed to increased water availability by biochars during the exceptionally dry growing season. In Viikki-2, the biochar increased plant available water in the upper soil layer (2.5–7.5 cm), right after application in 2011 (Tammeorg et al., 2014b), but this effect faded with time, which might also be due to the downward movement of biochar particles (**I**). The plant roots might have been able to take up water retained by those biochars in the lower soil layer. In a parallel study in Qvidja, plant available water has been found to increase in the biochar treatments that include soil samples taken in autumn 2018 (Peltokangas et al., Unpublished).

4.4.3 EFFECTS OF BIOCHAR ON N_2O EMISSIONS AND SOIL PROPERTIES

The percentage difference in the emissions of N_2O between the biochar and (fertilized) control treatments (ΔN_2O) correlated negatively with soil silt content, which indicates that the reduction in N_2O emissions by biochars is greater in soils with higher silt content (**IV**). The N_2O emissions tended to be smaller in the biochar treatments in Qvidja and Viikki-1 fields, where the soils had higher silt contents. In line with this, Hüppi et al. (2016) also found that biochar suppressed N_2O emissions more in silty soil compared to sandy soil. Similarly, the effectiveness of biochars to reduce N_2O emission in silty or loamy soils was also reported in meta-analyses (Liu et al., 2018; Liu et al., 2019a). Soils containing high silt contents usually have weak structures and are thus prone to soil compaction (Horn et al., 1995), creating anaerobic conditions favoring denitrification and N_2O production. The addition of biochars to such soils can increase aggregate stability (Soinne et al., 2014; Omandi et al., 2016; Heikkinen et al., 2019) and soil aeration (Blanco-Canqui, 2017) that might help to reduce overall denitrification and N_2O production (Rogovska et al., 2011).

Conversely, ΔN_2O had a significant positive correlation with initial soil C content (**IV**), indicating that the reduction in N_2O emissions by biochars is lower in soils with higher initial soil C contents. This might be attributed to the potential of biochars to increase the mineralization of SOM (Luo et al., 2011; Zimmerman et al., 2011; Nelissen et al., 2012; Singh and Cowie, 2014; Fiorentino et al., 2019). The increase in mineralization of SOM by biochars was also indicated in the short-term greenhouse experiment (section 4.3.3, **II**). The N bound in organic matter may become available for microbes during mineralization, and can eventually be released as N_2O via nitrification and denitrification processes (Kammann et al., 2017; Guenet et al., 2021).

5 CONCLUSIONS

Based on two longer-term field experiments (7–8 years since biochar application), two shorter-term field experiments (2 years since biochar application) and a ^{15}N labeling greenhouse experiment, it was observed that overall, biochars had either no effect or a slight positive effect on agricultural production and environmental benefits in boreal agricultural soils. The main conclusions are summarized below:

1. A single application of wood-based biochars has a limited effect on plant growth over the time span of eight years in both nutrient-poor and fertile boreal soils. In fertile boreal Stagnosol, biochar increased plant growth only in two instances, which were both linked to the pre-crop effect by N_2-fixing crops in the previous growing season. Such synergistic interactions of biochar and pre-crop effect need further exploration.
2. The consistently increased plant uptake of K and reduced plant availability of Al and Na observed in this research indicate that wood-based biochars could alleviate K limitation and may relieve the Na and Al toxicity stress of plants.
3. The increased plant contents of nutrients/elements (P, K, Mg, S, Al, Cd, Cu, Fe, and Ni) with time caused by biochars is in line with the increased ability of biochars to retain nutrients. This is a result of changes in their surface properties due to field-aging or release of nutrients contained in biochars as they weather. Conversely, the reduced plant content of Mn with time signifies that wood-based biochars can act as a source of Mn to plants in the short-term, but this effect fades over time. Further studies comparing the properties of field-aged and fresh archived biochar particles will facilitate verifying and understanding the mechanism behind increased nutrient retention by field-aged biochar.
4. The fading of the biochar effect on the physical and hydrological properties of topsoil in the long-term suggests that, with time, biochar pores are filled with clay and soil organic matter, or the biochar particles are physically fragmented and lost either due to mineralization, the downward movement of biochar in the soil profile, or wind/water erosion. Further studies to quantify the amount of biochar left in the topsoil and subsoil will help to verify whether the loss was due to mineralization or downward movement of the biochar.
5. The ability of biochars to retain nitrate explains the increased plant N uptake and reduced N leaching in both the greenhouse and the clayey field two years after the biochar application. The nitrate retaining ability of biochars, associated with the specific surface area, is an important property that enhances agricultural and environmental benefits. The optimization of biochar manufacturing and post-treatment processes need to be explored further in order to promote the nitrate retaining

ability. In addition, understanding the mechanisms behind nitrate retention by biochar also requires further study.

6. In the short-term, biochars may increase the loss of fertilizer NH_4^+ *via* NH_3 volatilization because of the increased soil pH. On the contrary, increased plant uptake and soil retention of fertilizer NO_3^- indicate the nitrate capturing ability of biochars. In addition, biochars could increase the plant availability N *via* increased mineralization of soil organic N in the short-term.
7. No clear effects of biochars were observed on the fluxes of N_2O and CH_4 from boreal agricultural soils. However, biochars tend to reduce N_2O flux during the peak emission period. The potential of biochars to reduce N_2O flux seemed higher on soil with higher silt content and lower initial C content. The gas flux measurements carried out during an extremely dry growing season might have concealed the true ability of biochars to reduce N_2O emission, which highlights the need for further measurements over multiple growing seasons and soil types to confirm the effectiveness of biochars in reducing N_2O emission.
8. Reduced yield-scaled emissions of N_2O and CH_4 from the coarse-textured soil after seven years of application suggest the potential of wood-based biochars for enhanced crop production in the long-term without increasing the emissions of non-CO_2 GHG to the atmosphere.

Over seven or eight years of field experimentation, no negative effects of biochars on agriculture and environment were detected. Hence, it appears that soil biochar application serves as a safe tool for increasing soil C sequestration. However, no consistent long-term improvement of crop yield and enhancement of environmental benefits such as reduced GHG emissions and N leaching can be expected after a single application of nutrient-poor wood-based biochars in boreal soils. Therefore, future studies should focus on the subsequent application of biochars, especially nutrient-rich ones such as co-composted biochars for a consistent increase in both soil carbon sequestration and crop yield.

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