Agriculture, Ecosystems and Environment 316 (2021) 107454

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

journal homepage: www.elsevier.com/locate/agee

Long-term effects of softwood biochar on soil physical properties, greenhouse gas emissions and crop nutrient uptake in two contrasting boreal soils

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ARTICLE INFO

Keywords:
Biochar
Field aging
Greenhouse gases
Plant nutrients
Soil physical properties

ABSTRACT

Biochars (BC) have tremendous potential in mitigating climate change, and offer various agricultural and environmental benefits. However, there is limited information about the long-term effects of added biochars particularly from boreal regions. We studied the effects of a single application of softwood biochars on two contrasting boreal agricultural soils (nutrient-poor, coarse textured Umbrisol and fertile, fine-textured Stagnosol), both with high initial soil organic carbon contents, over eight years following the application. We focused on plant nutrient contents and nutrient uptake dynamics of different field crops over these years, as well as on soil physical properties and greenhouse gas emissions during seven to nine growing seasons. We found that, added biochars had minor long-term effects on the crop biomass yield, plant nutrient contents and plant nutrient uptake in both soil types. In terms of crop biomass yields, significant biochar × fertilization interactions were observed in barley (in 2013) and peas (in 2016), three and six years after the application of biochar in Stagnosol, respectively. In both cases, the biochar combined with the normal fertilization rate (100% of the recommended value) significantly increased crop biomass yield compared to corresponding fertilization treatment without biochar. However, the biochar had no effect at a lower fertilization rate (30% of the recommended value). Similar significant biochar × fertilization interactions were observed for several plant nutrient contents for peas in 2016, and for uptake for both barley in 2013 and peas in 2016. Thus, the ability of biochar to enhance the supply of nutrients to plants and hence to improve the crop biomass yield exists in boreal conditions, although these effects were minimal and not consistent over the years. Biochar notably increased plant K content, and also increased K:Mg ratio in plant biomass, suggesting a possible antagonistic effect of K on Mg in Umbrisol. Similar K antagonism on Na was observed in Stagnosol. The applied biochar also reduced the plant content and uptake of Al and Na in several years in Stagnosol. Furthermore, we found that, increased plant Mn content with biochar in the initial years subsequently declined over the following years in Umbrisol. On the other hand, the relative plant contents of Cd and Ni in Umbrisol, and P, K, Mg, S, Al, Cu, Fe and Ni in Stagnosol increased over the years. Despite these increased plant contents, no significant improvement was observed in crop biomass yield by added biochar over the years. The enhanced plant available water and reduced bulk density previously reported during the initial years were faded in long-term, likely due to dilution of biochar concentration in topsoil. However, the potential of biochar to affect N_2O emission persisted, even seven years after the application.

1. Introduction

Biochars have been well acknowledged for their potential to enhance carbon sequestration and thus mitigate climate change. However, from a farmer's perspective, the main motivation for applying a biochar lies within its ability to enhance nutrient availability and crop yields. Numerous studies have been carried out in different regions of the world to assess these effects of biochar. The results have revealed that biochar application may yield varying results depending on the feedstock material, pyrolyzing temperature, soil properties and climate (Jeffery et al.,

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https://doi.org/10.1016/j.agee.2021.107454
Received 29 July 2020; Received in revised form 15 March 2021; Accepted 10 April 2021

2017). The highest improvements of crop yields by added biochars have been found in tropical and sub-tropical soils, which are usually characterized by low carbon content and cation exchange capacity (CEC), high acidity and coarse texture (Crane-Droesch et al., 2013; Jeffery et al., 2017; Liu et al., 2019). In contrast, boreal soils have relatively higher carbon content, typically more than 3% (Heikkinen et al., 2013), and go through continuous freeze-thaw cycles. The effects and processes of biochars in these soils can thus be arguably different from those in warmer climates, yet only few biochar studies have been conducted in these soils.

Biochars have high affinity to sorb nutrients, which tends to prevent the nutrients from leaching, keeping them available for plant uptake and hence enhancing the crop yield. Since biochars can persist in soils for thousands of years (Kuzyakov et al., 2014), a single application of biochar has potential to achieve long-term nutrient management goals. In addition, the aging of biochars in soil has been suggested to enhance nutrient availability and plant growth (Mia et al., 2017a). When aged in soil, modification of biochar surfaces could enhance the potential to withhold nutrients and keep them accessible for plant uptake (Cheng et al., 2006), which could further enhance the crop yield over time (Crane-Droesch et al., 2013). On the other hand, the fading positive effects of biochar on crop yield after a few seasons and the necessity of reapplication has been realized from a field condition in tropical region (Cornelissen et al., 2018). Therefore, the need for longer-term field experiments has been well addressed (Gao et al., 2019; Griffin et al., 2017; Tammeorg et al., 2017; Ye et al., 2020; Zhang et al., 2016). Some results from longer-term experiments (five or more years) have been reported from tropical and temperate climates (Blanco-Canqui et al., 2020; Futa et al., 2020; Giagnoni et al., 2019; Hardy et al., 2019; Kätterer et al., 2019; Quan et al., 2020; Williams et al., 2019). However, there remains a lack of sufficient longer-term experiments from different parts of the world, especially considering the wide variety of biochars and soils. Although the ability of biochars to produce beneficial crop yield in boreal conditions has been questioned (O'Toole et al., 2018; Soinne et al., 2020; Tammeorg et al., 2014a, 2014b), it is nevertheless important to investigate the possibility of long-term effects in terms of agricultural and environmental benefits of biochars as they age in the field. Once biochars are applied to soil, it is impossible to remove them, which further underscores the need to study the potential negative effects of biochars on soils in the longer-term.

The limitation of essential plant available macro- and micronutrients in soil may hinder crop yield. Investigating the effects of biochar on macro- and micro-nutrient contents in plant biomass may reveal potential positive and negative effects on nutrient balances in different crops. This information could subsequently be used to improve the use of biochars in relation to crop nutrition (Bornø et al., 2019). The effects of biochar on the bioavailability and plant nutrient uptake may vary depending on the soil type. In general, the positive effects on plant nutrient uptake are observed in acidic, nutrient poor, coarse textured soils (Akhtar et al., 2015; Alburquerque et al., 2013; Major et al., 2010), whereas these effects are less pertinent to neutral, nutrient rich, fine textured soils (Karer et al., 2013). Further, the enhancement of plant growth by biochar addition may also result from decrease in bioavailability of heavy metals in soil, and their uptake and translocation by plants. Moreover, the bioavailability and plant nutrient uptake effects of biochar could change over the time. Generally, biochar itself contains plant available macro- and micro-nutrients, which may vary depending on the feedstock (Ippolito et al., 2015; Ippolito et al., 2020; Kloss et al., 2012). Hence, during the initial period, a biochar itself can act as a fertilizer and contribute to supply such nutrients to plants. However, this effect fades over time because of subsequent plant uptake and leaching. For example, Spokas et al. (2014) noticed that the fresh biochar contained deposits of inorganic elements such as K, Ca, Cl, Mg, P, N, and O on its surfaces, which disappeared after shaking the biochar in water. Similarly, in a four-year tomato-corn rotation field experiment, Griffin et al. (2017) reported that walnut shell biochar improved corn production and availability of P, K and Ca, but only in the second year. In addition, the interaction of a biochar with added N or other fertilizers can also change over time. Biochars may induce short-term microbial N immobilization immediately following the application (Bruun et al., 2012; Tammeorg et al., 2012), which reduces the plant uptake of N. In contrast, field aging of the biochar particles modifies the surface properties, which can enhance the adsorption of ammonium ions (Mia et al., 2017b) and trapping of nitrate ions by biochar (Hagemann et al., 2017). Such field-aged biochars might slowly release the trapped nitrate ions, making them available for plant uptake for a longer time (Haider et al., 2016).

While most of the previous studies have focused on the effect of a biochar on single nutrients, there are only few studies that have addressed the effects on several macro- and micro-nutrients and their interactions. One such interaction is the biochar-induced antagonistic effects of K to the plant uptake of other cations. Biochars, particularly wood-derived ones, usually have high content of plant available K (Ippolito et al., 2015). The application of such a high K content biochar along with K fertilizer to fulfill plant needs, could lead to an excess of K in soil. In this case, K would replace other ions such as Ca, Mg, Na from soil colloids, leading to their deficiency in the soil and consequently to nutrient imbalance in plant biomass, which could be detrimental to plant growth (Jakobsen, 1993). The biochar-stimulated antagonistic effect of K on the uptake of both Ca and Mg in maize was observed in a pot experiment (Bornø et al., 2019). However, such biochar-induced interactions have not been sufficiently investigated in field conditions. Moreover, there is limited information about how the effects of a biochar on the bioavailability and uptake of macro- and micro-nutrients and their interaction develop over time as biochars age.

Agriculture sector is one of the major source of greenhouse gas (GHG) emissions into atmosphere, particularly N_2O. The application of synthetic N fertilizer into agricultural soils accounted for ~70% of total N_2O emissions during 2000–2014 (Xu et al., 2020). The short-term potential of biochars on reducing GHG from agricultural soils has further highlighted their role in mitigating climate change. Numerous studies have been carried out to understand the effects of various types of biochars on GHG emissions from various soil types and from different parts of the world. Although the direction and magnitude of GHG response to a biochar and the underlying reasons have not been clearly elucidated yet, several possible mechanisms have been postulated (Brassard et al., 2016). The recent meta-analyses carried out indicated that limited results are available from the long-term field experiments about the effects of biochar on GHG emissions (Borchard et al., 2019; Zhang et al., 2020a). In addition, some studies have questioned the effects of biochar on the suppression of GHG emissions in the long-term. For instance, Spokas (2013) reported that field aging of wood-derived and nut-shell biochars for two years negated the suppression of N_2O and enhanced CO_2 emissions, compared with the fresh biochar amendment in laboratory condition. In a meta-analysis, Song et al. (2016) reported that the suppression of N_2O emissions by biochar was prominent only during the early stages, and tended to weaken over time. However, most of the included studies were short-term (< 2 years) and in laboratory conditions. Similarly, Thers et al. (2020) reported that fresh, but not field-aged biochar (aged for 1.5 and 8 months) reduced N_2O emissions in laboratory condition; however no effect of fresh or field-aged (up to 3 years) biochars were observed on N_2O emissions in field condition. Nevertheless, there are enough grounds to propose that biochar can reduce GHG emissions after it has been applied to soil, even in the longer-term. For example, the nitrate ion trapped in the field-aged biochar pores may be inaccessible to microbial consumption (Haider et al., 2016), which prevents its denitrification and consequently results in lower N_2O emissions. Similarly, it has been claimed that some biochars permanently reduce soil bulk density by promoting soil aeration (Burrell et al., 2016), which in turn reduces CH_4 emissions. Biochar has also been reported to enhance inter-particle cohesion via organo-mineral interaction in the long-term (Quan et al., 2020), which promotes micro-aggregate stability and further stabilizes soil organic carbon, reducing CO_2 emissions even after several years of biochar application (Weng et al., 2017). However, there are limited studies reporting the persistence of the biochar effect on GHG fluxes in the longer-term (more than five years), even if considering the global importance of N_2O emissions to climate change, such studies are needed.

The positive effects of biochars on plant nutrient availability, crop yield and suppression of GHG emissions are directly related to the improvement of soil physical properties (Mukherjee and Lal, 2013). For example, Karer et al. (2013) reported a 10% increase in barley yield as a result of improved soil water holding capacity from application of a beech wood biochar in drought condition. Similarly, Karhu et al. (2011) reasoned that increased soil uptake of CH_4 after biochar addition was linked to improved soil aeration, thus decreasing anoxic conditions that favored CH_4 oxidation and/or decreased CH_4 production. However, the fate of the biochar modified soil physical properties in the long run is uncertain because the biochar particles may disappear over time (Kätterer et al., 2019). For instance, de la Rosa et al. (2018) reported that the physical fragmentation of biochar particles significantly increased, 11–27% of the initial C was lost from different biochars, and the mean residence time of several types of biochars was significantly less than expected, when aged in the field for about two years in Mediterranean climate. Spokas et al. (2014) also concluded that field aging led to physical disintegration of the biochar, which made it easily soluble and prone to leaching downward in soil profile by water infiltration.

In the present study, our aim was to fill the abovementioned knowledge gaps relating to the long-term effects of biochar application. Specifically, we studied the effects of softwood biochars on crop biomass yield, as well as plant nutrient contents and uptake for eight growing seasons after the incorporation of biochar in two boreal soils with contrasting fertilization and nutrient status. In addition, we aimed to unveil the effects of a single-dose application of biochar on the soil physical properties and GHG emission on seven to nine growing seasons after the biochar application.

2. Methods

2.1. Experimental sites, soil characteristics and weather conditions

The study focuses on data from the first eight growing seasons of two long-term ongoing field experiments conducted on contrasting boreal soils: a fertile Stagnosol with a sandy clay loam texture (2010–2017) and a nutrient deficient Umbrisol with a loamy sand texture (2011–2018) at the Viikki Research Farm, University of Helsinki, Finland (Table A.1). The long-term biochar experiments at these field sites were started in 2010 and 2011 with single-dose additions of softwood biochars into the Stagnosol field (Tammeorg et al., 2014a) and the Umbrisol field (Tammeorg et al., 2014b), respectively. Prior to the biochar application, both fields were cropped with small grains and the soil was tilled with conventional annual moldboard ploughing up to a depth of 25 cm for the preceding five years.

The growing season from 2011 to 2014 and 2016 received more precipitation compared to other growing seasons (May to September) and the long-term average of 1981–2010 (FMI, 2020; Fig. B.1). Since the plant samples were usually taken at the end of June or early July, the weather conditions in June are relatively important. June of 2010, 2013 and 2018 were drier, while that of 2012 and 2014–2017 were wetter than the long-term average (more than 10% difference compared to the 1981–2010 average). June of 2011 and 2013 were relatively hotter compared to the long-term average. It is also noteworthy that the precipitation during the early period of the growing season in May was considerably lower from 2016 to 2018 compared to the long-term average.

2.2. Experimental design

The experiments in both fields were set up with a split-plot design with four complete replicate blocks of treatments (plot area of 2.2×10 m^2) sown with combined drill resulting in simultaneous placement of seed and fertilizers into soil. In Stagnosol field, the experimental setup consisted three identically designed sub-experiments, which had different crops in all years except in 2013–2015 (Table A.2). The experimental factor in the main-plot was the biochar application rate [0, 5 and 10 Mg dry matter (DM) ha^{-1}]. The experimental factor in the sub-plot was the application rate of the compound fertilizer with three different levels [30%, 65% or 100% of the fertilizer levels recommended for the individual crops according to Viljavuuspalvelu Oy (2000)].

In the Umbrisol field, the experimental factor in the main-plot was similarly the biochar application rate (0, 5, 10, 20 and 30 Mg DM ha^{-1}) while that in the sub-plot was the fertilizer treatment with three different levels [unfertilized control, organic fertilizer (meat bone meal, MBM) and mineral (synthetic) fertilizer]. The organic and mineral fertilizers provided the same amounts of the most critical nutrients N and K on this high-P Umbrisol soil. The corresponding type and amount of fertilizers were applied during sowing of both fields except in 2014 and 2015 when no fertilizers were applied to the grasses grown at the Umbrisol field (Table A.3). In this paper, only the extreme treatments were considered i.e. “no” and “highest” BC application rates with 30% and 100% of the recommended fertilizer level in Stagnosol field and, “no” and “highest” BC application rates with all three-fertilizer treatments in Umbrisol (Table 1). Since 2016, the fertilization covered all the nutrient needs of crops regarding to N, P, K, S, Mg, B, Cu, Mn and Zn to the fertilized plots of Umbrisol field and to the 100% fertilizer level plots in Stagnosol field, whereas earlier, only the main nutrients N-P-K were taken into account during the fertilization (Tables A.3 and A.4). In 2018, the fertilization was arranged according to the needs of common flax (*Linum usitatissimum* L.) in the Umbrisol field, which was sown on 11 May 2018. However, due to exceptional drought during May–June, flax failed to establish, and barley was sown instead on 14 June 2018 without adding more fertilizers.

The neighboring main plots were separated by buffer plots of the same crop for minimizing biochar carryover. Integrated crop management practices were used, including the use of chemical herbicides, fungicides and pesticides when necessary (details in Tammeorg et al. in preparation). In 2016, the oats were infected with barley yellow dwarf virus in Umbrisol, otherwise there were no plant diseases severe enough to notably harm crop yields.

2.3. Biochar

The procedure about production and various properties of applied biochars along with the process of application in Stagnosol and Umbrisol were described in Tammeorg et al. (2014a) and Tammeorg et al. (2014c), respectively. Briefly, the biochar applied in the Stagnosol field was produced from debarked spruce and pine; the biochar applied in the Umbrisol field was produced from debarked spruce only. Both biochars were produced similarly by pyrolyzing the feedstock in a continuously running carbonizer (Preseco Oy, Lempäälä, Finland) at 550–600 °C. Air dried wood chips were fed into the reactor tube via an airtight system and subsequently moved by a screw conveyor through the hot region of the reactor tube in 10–15 min. The biochar was then cooled overnight in an airtight silo before grinding in a roller mill. The single-dose moistened biochar application was conducted with a sand spreader followed by its incorporation into the uppermost 10 cm soil layer by two opposite passes with a rotary power harrow in May 2010 and May 2011 in the Stagnosol and Umbrisol fields, respectively. The biochar applied to Umbrisol had almost 10 times higher specific surface area, but less ash content compared to that applied to Stagnosol (Table A.5). The contents of C, P, K, Mg and S in both biochars were almost identical while N and Ca contents were slightly higher in the biochar applied to Stagnosol. The

Table 1
Field experimental treatments and their coding.

Stagnosol Field				Umbrisol Field			
BC rate Mg ha^{-1}	Fertilization				Fertilization		
	30%	65%	100%	BC rate Mg ha^{-1}	Unfertilized Control	Meat Bone Meal	Mineral Fertilizer
				0	**B_0F_0**	**B_0F_{Org}**	**B_0F_{Min}**
				5	B_5F_0	B_5F_{Org}	B_5F_{Min}
0	**B_0F_{30}**	B_0F_{65}	**B_0F_{100}**	10	$B_{10}F_0$	$B_{10}F_{Org}$	$B_{10}F_{Min}$
5	B_5F_{30}	B_5F_{65}	B_5F_{100}	20	$B_{20}F_0$	$B_{20}F_{Org}$	$B_{20}F_{Min}$
10	**$B_{10}F_{30}$**	$B_{10}F_{65}$	**$B_{10}F_{100}$**	30	**$B_{30}F_0$**	**$B_{30}F_{Org}$**	**$B_{30}F_{Min}$**

“Bx” refers to the rate of biochar application (x is 0, 5, 10, 20 or 30). “Fy” refers to the fertilizer application rate (y is 30, 65 or 100) in Stagnosol field and type of fertilizer applied (y is 0 = control, Org = Meat Bone Meal or Min = Mineral) in Umbrisol field. Only the extreme treatment combinations i.e. the treatments with bold letters were considered for this study.

total inputs of nutrients/elements from biochar application at the highest rates to the fields are presented in Table A.6.

2.4. *Plant sampling and analysis*

Each year, the above ground biomass (AGB) of plants were sampled at the full flowering stage (usually at the end of June or early July) i.e. at growth stage 65 (Meier, 2001), within a 2 × 2 m^2 area at one end of the plots. The plants were cut with scissors at 2 cm above the soil surface from 3 × 30 cm of sowing row for cereals, and 3 × 50 cm for turnip rape, faba bean and peas. For grasses, the sampling was conducted using a 30 × 30 cm^2 sampling frame with a cutting height of 12 cm. The plant samples were dried in paper bags in oven at 60 °C for 72–96 h, and their dry mass was recorded to calculate the AGB. The samples were then ground and analyzed for C and N contents using VarioMax CN analyzer (Elementar Analysensysteme GmbH, Hanau, Germany). Furthermore, the plant samples were subjected to dry ashing by heating in a muffle furnace in which the temperature increased until it reached 500 °C within 2 h, and then maintained at this temperature for another 3 h. The plant samples were then cooled in a desiccator. For the extraction of plant elements, the samples were treated with 50 mL 0.2 M HCl and then boiled until the volume was less than 25 mL, cooled, and then Milli-Q water was added until the volume reached 50 mL again (Miller, 1998). The mixture was filtered through Whatman™ 589/3 filter paper (ashless) and analyzed for determining the concentration of the elements (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) after appropriate dilution. Three analytical replicates were included for each sample used in the plant elemental analysis. Blanks and known certified reference plant material (NIST® SRM® 1573a) were extracted and analyzed similarly like samples for quality assurance. The samples were extracted and analyzed in batches. The samples from each field replicate of each year and two blanks constitute a batch. Each batch of samples were introduced to ICP-OES in the same order - initial blank, samples, reference samples and final blank. After every two batches, internal quality control was ascertained by introducing known quality control samples to the ICP-OES.

The plant nutrient uptake was calculated by multiplying the concentration of a nutrient by AGB. The apparent nutrient use efficiencies (ANUE) were calculated for the Umbrisol field as:

$$\text{ANUE}(\%) = \frac{\text{NU}_\text{T} - \text{NU}_\text{c}}{\text{F}} \times 100 \tag{1}$$

ANUE is the apparent use efficiencies of N (NUE), P (PUE) and K (KUE); NU$_\text{T}$ is the total uptake of N/P/K (kg ha^{-1}) in the treated plots from 2011 to 2018; NU$_\text{c}$ is the average of total uptake of N/P/K (kg ha^{-1}; from 2011 to 2018) from plots where neither biochar nor fertilizers were added (n = 4); F is the total N/P/K fertilizer applied (kg ha^{-1}) from 2011 to 2018, which also includes total N/P/K input of biochar in the biochar treated plots (Liu et al., 2021).

2.5. *Greenhouse gases and soil physical properties*

The fluxes of GHGs (CO_2, N_2O, CH_4) were measured in situ using an automated Fourier Transform Infrared Trace Gas Analyzer (FTIR-TGA) (Gasmet DX4015, Gasmet, Helsinki, Finland). In 2017, GHG emissions were measured 16 and 12 days after fertilization in the Stagnosol and Umbrisol fields, respectively, and again 20 and 18 days after harvesting in the Stagnosol and Umbrisol fields, respectively. In 2018, GHGs were measured two times after fertilization – after 5 and 9 days in the Stagnosol field, and after 18 and 22 days in the Umbrisol field. They were measured again 21 and 3 days after harvesting in Stagnosol and Umbrisol, respectively. The concentrations of the gases were measured for 10 min after deploying the opaque chamber in the field. The aluminum chamber used was cylindrical in shape (27 cm height, 31.5 cm diameter; total volume 0.0196 m^3) with an electric fan attached inside to circulate the air during measurement. The gas sampling probe was air-tightly inserted inside the chamber from which, the air was continuously pumped to the analyzer and returned back to the chamber via the outlet after the analysis. The first two minutes of measurements were discarded to avoid the probable effects of immediate chamber deployment on gas concentration and carry over effect from previous measurements. The flux calculation was made by fitting a linear regression of gas concentration vs. time of measurement.

Four undisturbed soil samples (from 2.5 to 7.5 cm) per plot were taken into steel cylinders after harvesting in the autumn of growing season 2017 for the determination of bulk density, porosity and the water retention curve (WRC). The WRC was determined by using the sand-box method for pF 1.5 and 1.8, and the pressure plate method for pF 2, 2.7, 3, 3.4 and 4.2 (Dane and Hopmans, 2002). The pF 2 corresponds to the matric water potential of − 10 kPa [pF = log (h), where h is the matric suction head in cm of water column]. The same samples were used to calculate the plant available water content [AWC; as the difference in soil water content at field capacity (pF 1.8) and wilting point (pF 4.2)] and bulk density. The total porosity was calculated from bulk density assuming a density of 2.65 g cm^{-3} for soil particles. The greenhouse gases and soil physical properties were measured only from one sub-experiment of the Stagnosol field due to limited resources.

2.6. *Calculation and data analysis*

The effects of experimental treatments were tested with linear mixed effects model using “lmer” function under the “lme4″ library in R (Bates et al., 2015; R Core Team, 2018). “Biochar”, “fertilizer” and their interactions were used as fixed factors, while “replicate” and its interactions were used as random factors. In the case of the Umbrisol field, the highly variable initial soil carbon content was included as a co-variate in the model. The assumptions of homogeneity and normality were checked via “residuals vs. fitted values” plots and “standardized residuals vs. theoretical quantiles” plots, respectively. For those cases that deviated from these assumptions (Table A.7), a Box-Cox transformation was applied (Box and Cox, 1964) to approach the assumptions. *Post hoc* tests were computed using “emmeans” function (“emmeans” package; Lenth, 2019) with the Tukey method for P-value adjustments utilizing Satterthwaite’s approximation for degrees of freedom and a significance level of $p < 0.05$ specified in the “cld” function (“multcompView” package; Graves et al., 2019). The data was analyzed at 5% level of significance ($p < 0.05$). Whenever relevant, the significance at $p < 0.1$ was also considered.

The linear mixed effects model did not provide readily comparable information about how the crop biomass and plant nutrient contents progressed over time in response to biochar. Furthermore, the heterogeneity among crops in different years and sub-experiments obstructed the comparison over the years, which was overcome by normalization. The above ground biomass yield and plant nutrient contents values were normalized to compute the relative crop yield and plant elemental contents. The normalization truncated the variation due to different crops and environmental conditions at different years and sub-experiments. For the normalization, the corresponding individual values of biochar treatment plots with 100% fertilizer level (i.e. $B_{10}F_{100}$ for Stagnosol, $B_{30}F_{Min}$ for Umbrisol) was divided by the average of the control with the same fertilization but without biochar addition (for the respective sub-experiment) for each year. Thus, the treatment with no biochar with 100% fertilizer level (i.e. B_0F_{100} for Stagnosol, B_0F_{Min} for Umbrisol) was considered as the control for normalization. Regression analysis was carried out between the normalized values (relative crop biomass yields or elemental contents) vs. year. The statistical test was carried out to test the null hypothesis that the regression coefficient is zero i.e. no change in normalized value with time.

$$\text{Normalized value} = \frac{BC_{30}F_{Min}}{BC_0F_{Min}}(\text{for } \mathit{Umbrisol}) \quad \text{or } \frac{BC_{10}F_{100}}{BC_0F_{100}}(\text{for } \mathit{Stagnosol}) \tag{2}$$

Principal Component Analysis (PCA) was carried out for the plant elemental contents. Since the plant elemental contents are compositional, they were center log ratio transformed using the “robCompositions” package in R (Bornø et al., 2019). Since Al and Cr contained numerous zero values for Stagnosol, they were excluded from the PCA. The stoichiometric ratios for K:Ca, K:Mg, K:Na were calculated for the treatments with mineral fertilizer application: “BC_0F_{min}” and “$BC_{30}F_{min}$” for the Umbrisol field, and the 100% fertilization treatments: “BC_0F_{100}” and “$BC_{10}F_{100}$” for the Stagnosol field. The difference in these ratios with and without biochar were tested using a two-sample *t*-test.

3. Results

3.1. Crop biomass yield

No effects of biochar or biochar × fertilizer interaction were observed on AGB yield in any of the fields with two exceptions: barley in 2013 (sub-experiment 3) and peas in 2016 (sub-experiment 1) in Stagnosol (Figs. 1 and 2). In both cases, biochar × fertilizer interaction was significant ($p < 0.05$), and the effect of biochar was prominent only at the higher fertilization rate.

In Umbrisol, the effects of fertilization were significant in the growing seasons from 2011 to 2013 and in 2018, whenever the crop was either wheat or barley. Both organic and mineral fertilizers improved the crop biomass yield compared to the control; the mineral fertilizer performed slightly better than the organic fertilizer. During 2018, the fertilization effects were low compared to those in 2011–2013. Similarly, in Stagnosol, higher fertilization rate significantly improved the biomass yield of barley (2013 in all sub-experiments and 2017) and wheat (in 2010–2012 wheat - turnip rape - faba bean rotation, even if only tentatively significant at $p < 0.10$ in 2010) compared to the lower fertilization rate. Moreover, the biomass yield of turnip rape in 2012 was significantly improved with the higher fertilization.

3.2. Contents and uptake of elements and nutrient use efficiency by plants

The effects of biochar on plant elemental contents (Tables 2a; C.1–C.4) or uptake (Tables 2b; D.1–D.4) were minimal and inconsistent. Most noticeably, biochar enhanced the plant K content in Umbrisol, while reduced the plant content and uptake of Na and Al in Stagnosol. In Umbrisol, biochar enhanced plant K content in five out of the eight growing seasons ($p < 0.1$), even in 2014 and 2015 when no fertilizers were applied. The plant K uptake was also increased by biochar in 2014 and 2015 (in 2015, K uptake was increased by 27%, but not statistically significant $p = 0.160$, Table D.4). The contents and uptake of some macro- and micro-elements were either increased or decreased by

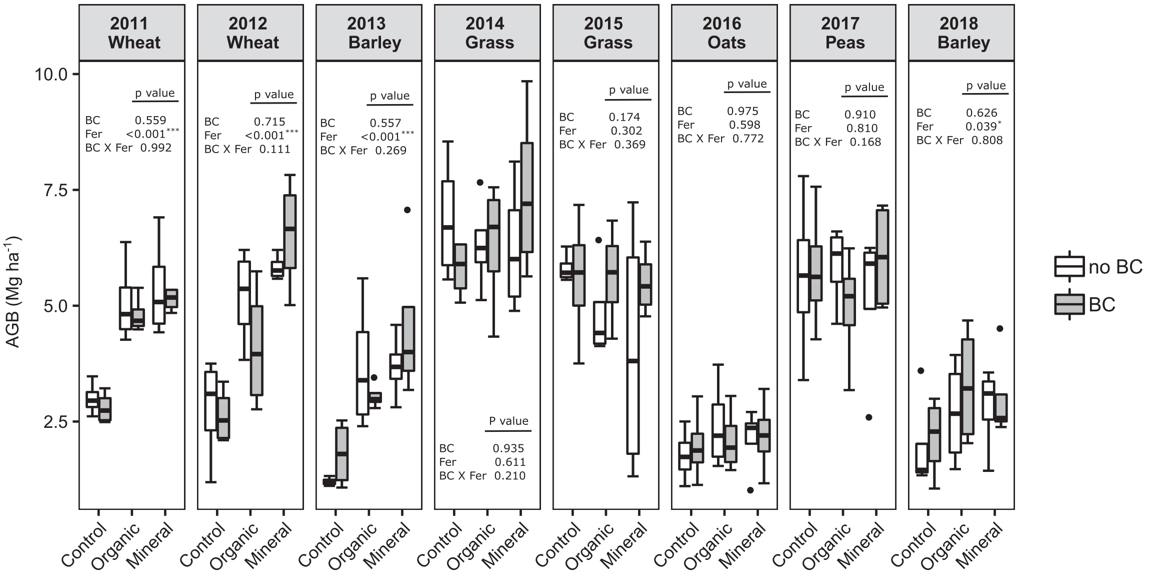


Fig. 1. Crop biomass yield (Mg ha^{-1}) in the experimental treatments [unfertilized control, organic fertilization or mineral fertilization (Fer), each without or with 30 Mg ha^{-1} added biochar (BC)] and statistical significance of experimental factors of the Umbrisol field in 2011–2018. The line inside the box represents the median, the top and bottom of the box represent third (Q3) and first (Q1) quartiles respectively, top whisker is Q3 + 1.5 IQR and bottom whisker is Q1–1.5IQR, values beyond this range of whiskers are plotted as dots.

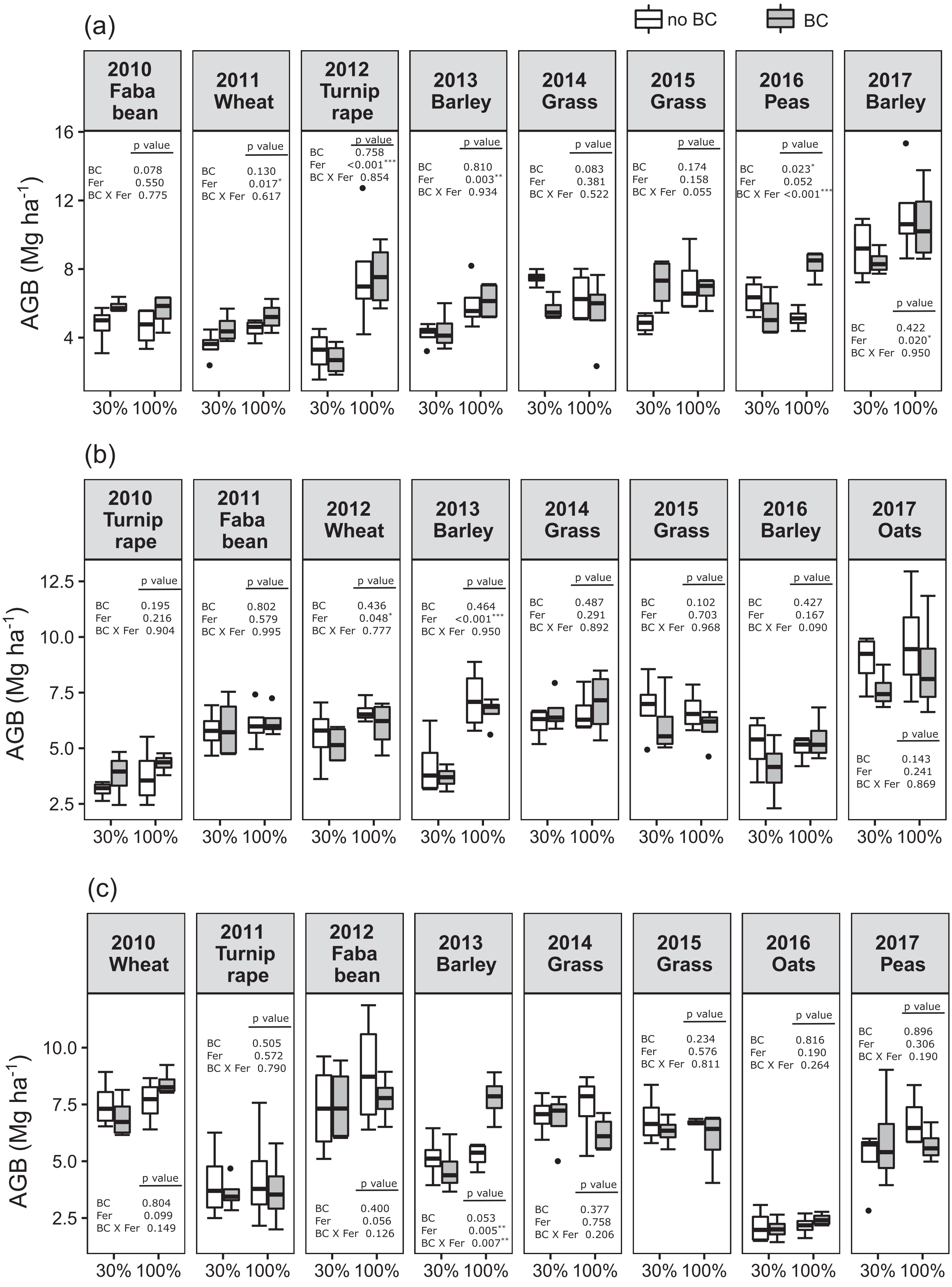


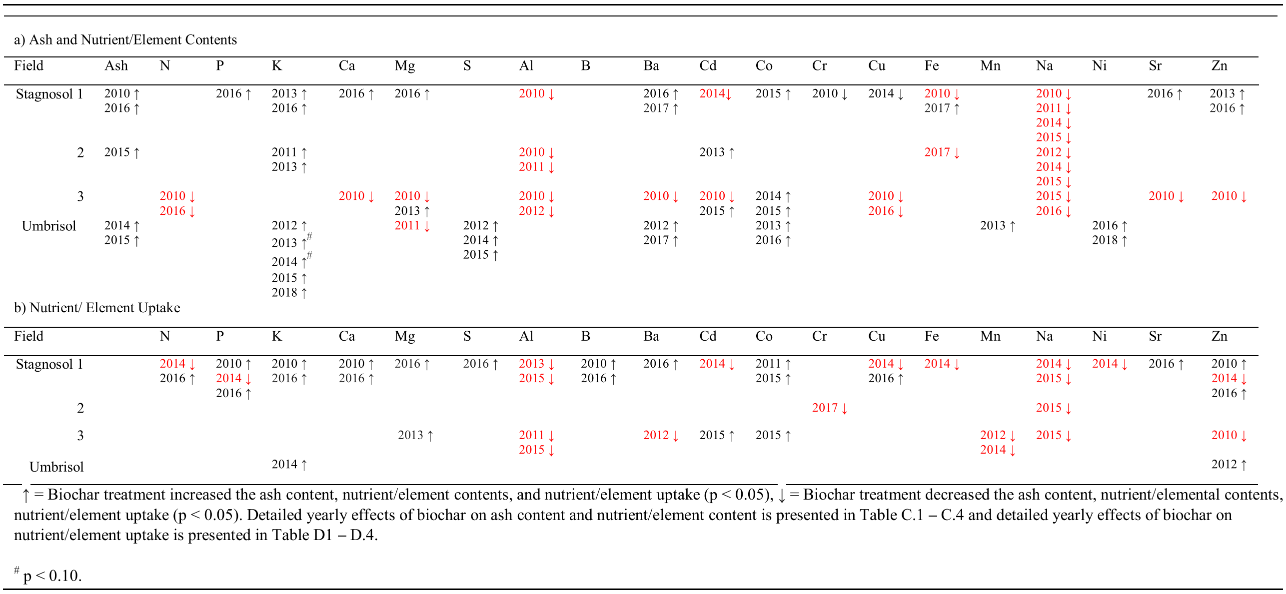
Fig. 2. Crop biomass yield in the experimental treatments [30% or 100% of recommended fertilizer level (Fer), each without or with added 10 Mg ha^{-1} biochar (BC)] and the statistical significance of experimental factors at sub-experiments 1 (a), 2 (b) and 3 (c) of the Stagnosol field in 2010–2017. The information about the box and whiskers is same as in Fig. 1.

biochar, depending on the crop type (Table 2). In the first year of biochar application in the Sub-experiment 3 of the Stagnosol field, biochar decreased the plant contents of several elements (Table C.3).

The effects of fertilization on both the plant contents (Tables C.5–C.8) and the plant uptake (Tables D.5–D.8) were prominent, but not persistent throughout all growing seasons. The uptake of several macro- and micro-elements improved with fertilization in Umbrisol, and with the higher (100% of recommended level) fertilization level in Stagnosol when the crop was either wheat or barley, except in 2010 in Stagnosol and 2016 in Umbrisol. Besides wheat and barley, fertilization

Table 2

Experimental years showing statistically significant effects of biochar on the ash and nutrient/element contents of plants (a), and nutrient/element uptake (b) in the Stagnosol and Umbrisol fields.



a) Ash and Nutrient/Element Contents

Field	Ash	N	P	K	Ca	Mg	S	Al	B	Ba	Cd	Co	Cr	Cu	Fe	Mn	Na	Ni	Sr	Zn
Stagnosol 1	2010 ↑ 2016 ↑		2016 ↑	2013 ↑ 2016 ↑	2016 ↑	2016 ↑		2010 ↓		2016 ↑ 2017 ↑	2014↓	2015 ↑	2010 ↓	2014 ↓	2010 ↓ 2017 ↑		2010 ↓ 2011 ↓ 2014 ↓ 2015 ↓		2016 ↑	2013 ↑ 2016 ↑
2	2015 ↑			2011 ↑ 2013 ↑				2010 ↓ 2011 ↓			2013 ↑				2017 ↓		2012 ↓ 2014 ↓ 2015 ↓			
3		2010 ↓ 2016 ↓			2010 ↓	2010 ↓ 2013 ↑		2010 ↓ 2012 ↓		2010 ↓	2010 ↓ 2015 ↑	2014 ↑ 2015 ↑		2010 ↓ 2016 ↓			2015 ↓ 2016 ↓		2010 ↓	2010 ↓
Umbrisol	2014 ↑ 2015 ↑			2012 ↑ 2013 ↑$^{\#}$ 2014 ↑$^{\#}$ 2015 ↑ 2018 ↑		2011 ↓	2012 ↑ 2014 ↑ 2015 ↑			2012 ↑ 2017 ↑		2013 ↑ 2016 ↑				2013 ↑		2016 ↑ 2018 ↑		

b) Nutrient/ Element Uptake

Field	N	P	K	Ca	Mg	S	Al	B	Ba	Cd	Co	Cr	Cu	Fe	Mn	Na	Ni	Sr	Zn
Stagnosol 1	2014 ↓ 2016 ↑	2010 ↑ 2014 ↓ 2016 ↑	2010 ↑ 2016 ↑	2010 ↑ 2016 ↑	2016 ↑	2016 ↑	2013 ↓ 2015 ↓	2010 ↑ 2016 ↑	2016 ↑	2014 ↓	2011 ↑ 2015 ↑		2014 ↓ 2016 ↑	2014 ↓		2014 ↓ 2015 ↓	2014 ↓	2016 ↑	2010 ↑ 2014 ↓ 2016 ↑
2												2017 ↓				2015 ↓			
3					2013 ↑		2011 ↓ 2015 ↓		2012 ↓	2015 ↑	2015 ↑				2012 ↓ 2014 ↓	2015 ↓			2010 ↓
Umbrisol			2014 ↑																2012 ↑

↑ = Biochar treatment increased the ash content, nutrient/element contents, and nutrient/element uptake ($p < 0.05$), ↓ = Biochar treatment decreased the ash content, nutrient/elemental contents, nutrient/element uptake ($p < 0.05$). Detailed yearly effects of biochar on ash content and nutrient/element content is presented in Table C.1 – C.4 and detailed yearly effects of biochar on nutrient/element uptake is presented in Table D1 – D.4.

$^{\#}$ $p < 0.10$.

↑ = Biochar treatment increased the ash content, nutrient/element contents, and nutrient/element uptake ($p < 0.05$), ↓ = Biochar treatment decreased the ash content, nutrient/elemental contents, nutrient/element uptake ($p < 0.05$). Detailed yearly effects of biochar on ash content and nutrient/element content is presented in Tables C.1–C.4 and detailed yearly effects of biochar on nutrient/element uptake is presented in Tables D1–D.4.

# $p< 0.10$.

improved the uptake of several elements by turnip rape in 2012, peas in 2016 and oats in 2017 in Stagnosol. Higher fertilization also improved the uptake of K, S, Cu and Zn by oats in 2016.

Biochar × fertilization interactions were inconsistent and seldom statistically significant (Tables E.1 and E.2) in either field for both plant contents and uptake. Some noticeable biochar × fertilizer interaction was found in Stagnosol where biochar had no or negative effects at the lower fertilization rate, while a positive effect on plant nutrient contents and ash content was observed at the higher fertilization rate (Table E.3). Most of those interactions were significant in the case of peas in 2016 (for ash content and plant contents of P, K, Mg, S, Ba and Sr; Table E.4). Biochar also increased N content by about 32% at the higher fertilization rate, but was not statistically significant. Similarly, the biochar × fertilization interaction was significant for the uptake of N, P, K, Ca, Mg, S, B, Ba, Cu, Mn, Sr, Zn in peas in 2016 and for the uptake of N, P, K, Ca, Mg, S, Ba, Fe, Mn, Sr, Zn in barley in 2013 in Stagnosol (Table D.4).

Biochar application along with mineral fertilizer significantly increased NUE and KUE compared to its application along with organic fertilizer ($p < 0.05$, Fig. 3). The biochar treatment with mineral fertilizer increased average NUE and KUE by 45% and 74%, respectively, compared to the mineral fertilizer only treatment even though the differences were not statistically significant. In overall, mineral fertilization had significantly higher NUE, PUE and KUE compared to organic fertilization ($p < 0.05$).

3.3. *Temporal change in the elemental composition of plants by added biochar*

The regression of normalized values of plant elemental contents against the time showed that biochar increased the plant contents of P, K, Al, Cu and Fe over the years in Stagnosol (Fig. 4). While considering also the tentatively significant results at $p < 0.1$, plant contents of Mg, S and Ni also increased over the years. In Umbrisol, biochar significantly increased plant Cd ($p < 0.10$) and Ni contents ($p < 0.001$) over the years while it significantly decreased plant Mn content ($p < 0.05$) (Fig. 5). Biochar did not affect the crop biomass yield (AGB) over the years in both fields. Although the regression was not significant, the average normalized value lines for AGB, N, P, K, Ca and S were always greater than or equal to 1 for Umbrisol.

3.4. *Relationships between nutrients and other elements taken up by plants*

PCA analysis showed that plant elemental content data was well clustered according to crop type rather than the treatments applied. For Stagnosol, PC1 and PC2 explained 45.89% and 20.31% of the variation, respectively (Fig. 6). Most notably, the vectors of K and Na were in opposite directions, indicating a negative correlation. In Umbrisol, PC1 and PC2 explained 42.04% and 25.78% of the variation, respectively (Fig. 7). The vectors of B, Mg, Ni, Sr, Ca and Co were pointed to the right while those of Na, Fe, Cd, Cr, Ba, Cu, P and K were pointed to the left.

There was no difference in plant K:Ca ratios in any of the fields when biochar vs. no biochar treatments were compared across all the years (data not shown). This was also observed for the K:Mg ratios for the Stagnosol field. However, in Umbrisol, biochar treatment had a significantly higher K:Mg ratio [Fig. B.2; 2/8 cases with $p < 0.05$ (2013 and 2018), 6/8 cases with $p < 0.1$ (2011–2013, 2015, 2016, 2018)]. Similarly, in the Stagnosol field, biochar treatments had noticeably higher K:Na ratios than no biochar treatments (Fig. B.3).

3.5. *Soil physical properties and greenhouse gas emissions*

The applied softwood biochars had no effect on the soil physical properties (Table F.1) and water retention characteristics (Fig. B.4). In addition, biochar, fertilization, or biochar × fertilization interaction did not affect the emissions of greenhouse gases (CO_2, CH_4 and N_2O) from soils in Stagnosol field except during one of the measurements in 2018 after sowing (2018–05–25) where the higher fertilization had reduced CO_2 emissions compared to the lower fertilization (Fig. 8).

In Umbrisol, the organic fertilization had significantly higher CO_2 emission than the control and mineral fertilization after sowing in 2018

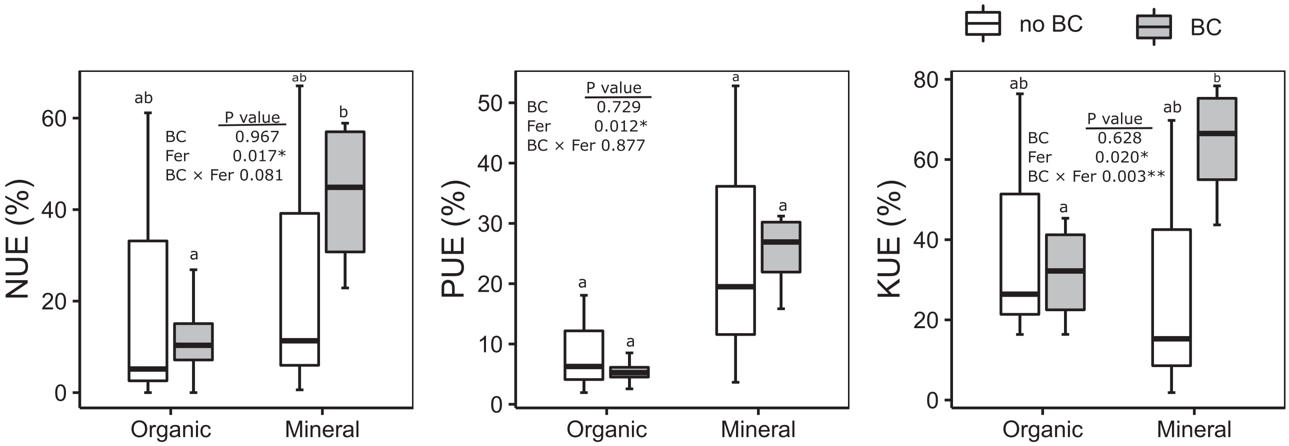


Fig. 3. Overall use efficiencies of N (NUE), P (PUE) and K (KUE) in the experimental treatments [organic fertilization or mineral fertilization (Fer), each without or with 30 Mg ha^{-1} added biochar (BC)] and statistical significance of experimental factors of the Umbrisol field. The information about the experimental treatments and the box and whiskers is same as in Fig. 1.

(on 2018-05-20) (Fig. 8). Similarly, the organic fertilization had significantly higher N_2O emission (on both 2018-05-20 and 2018-05-24) than the control; the difference between organic and mineral fertilization was not statistically significant. In Umbrisol, biochar treatment significantly reduced N_2O emission by an average of about 30% compared to the no biochar treatment on 2018-05-20. The

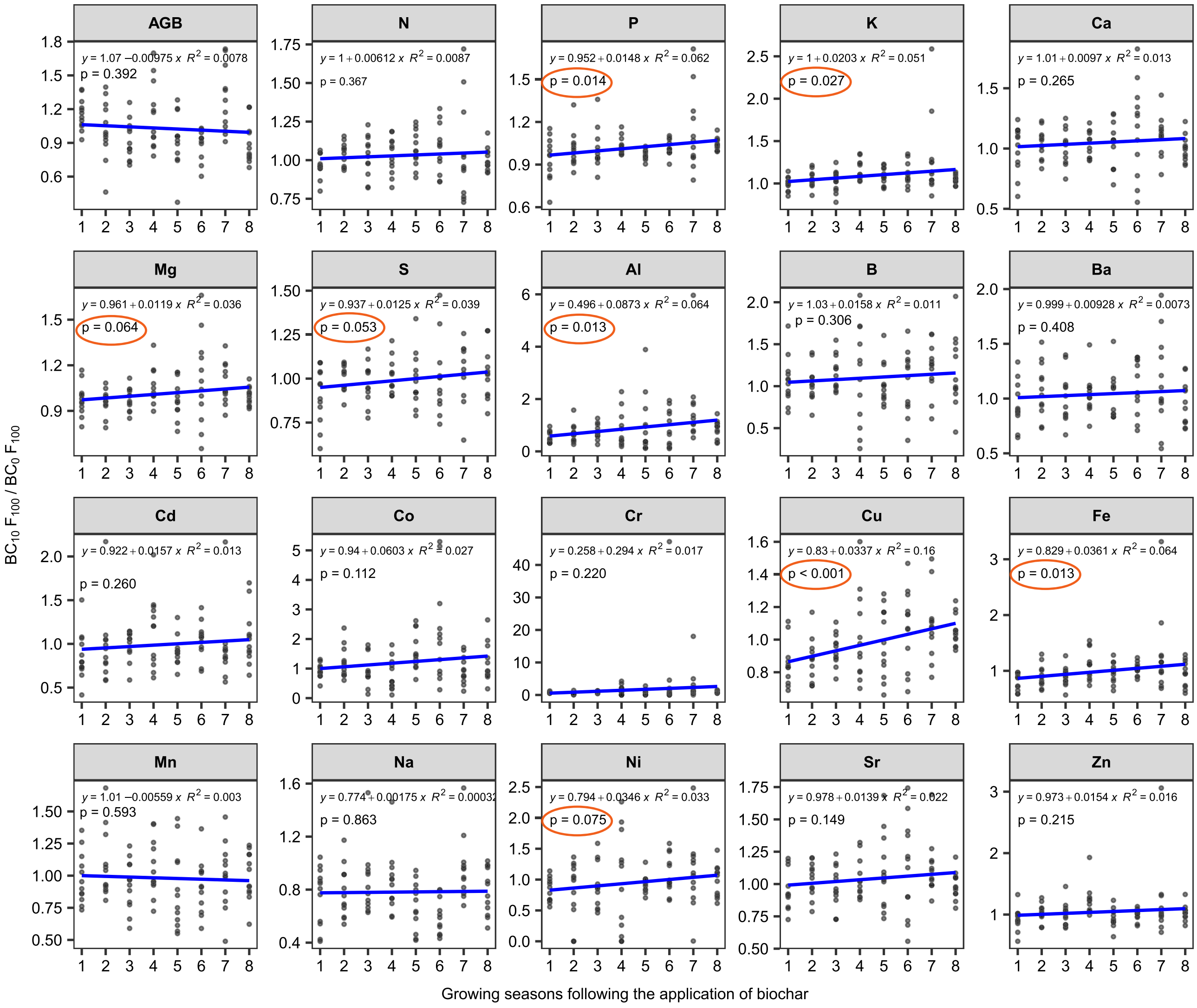


Fig. 4. The effects of biochar on the relative AGB and plant elemental contents over time in Stagnosol. The values are across three sub-experiments, thus n = 12.

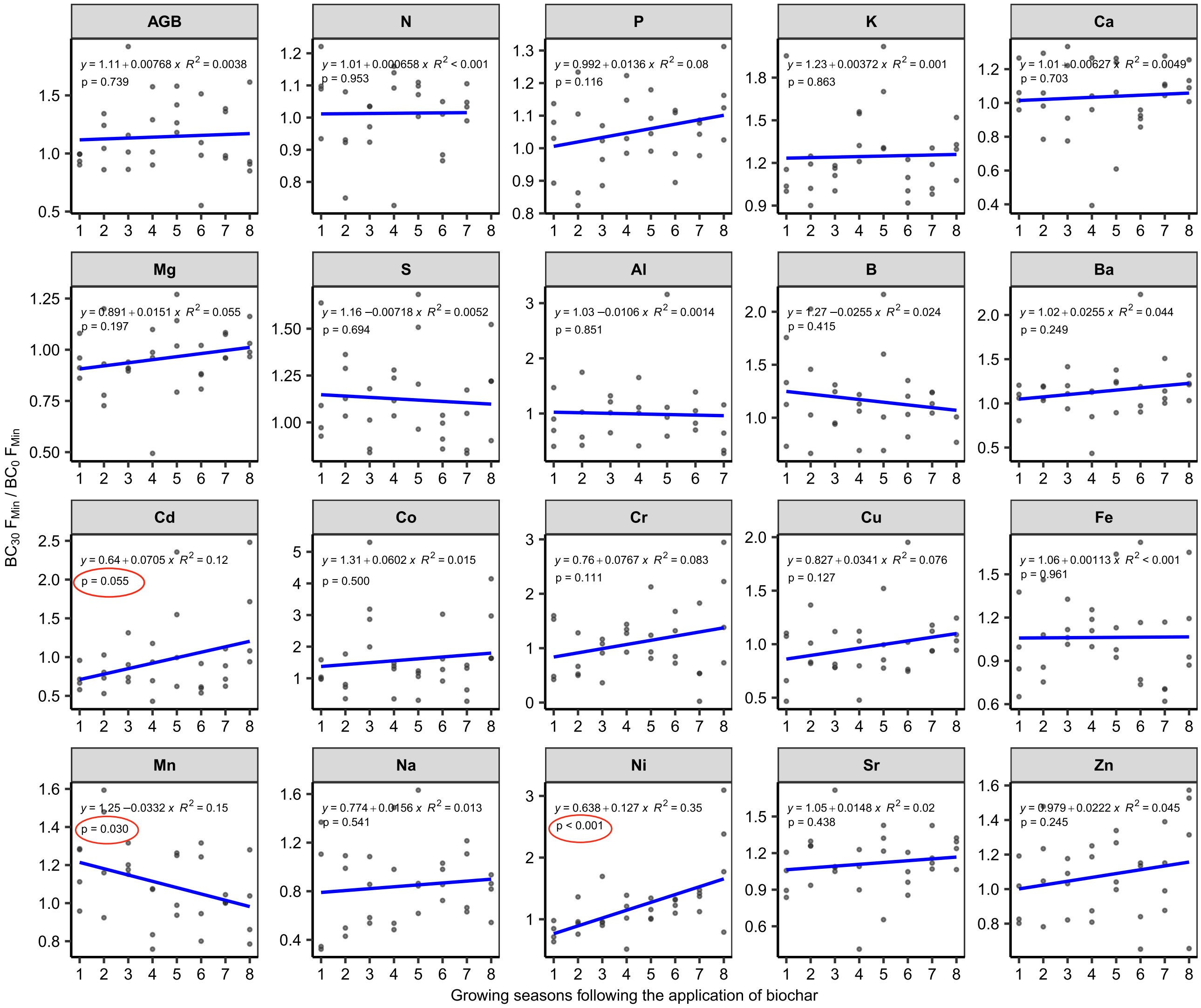


Fig. 5. The effects of biochar on the relative AGB and plant elemental contents over time in Umbrisol.

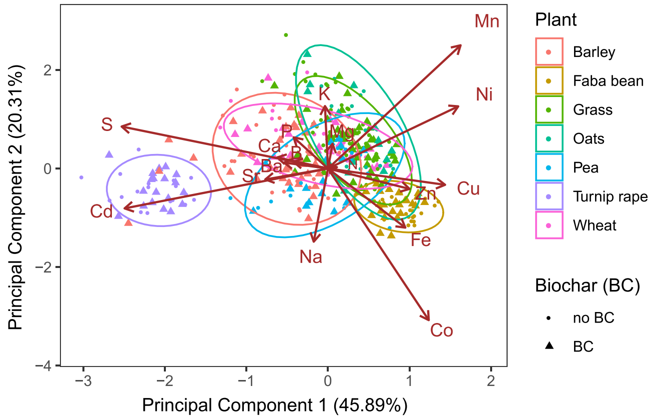


Fig. 6. Principal Component Analysis of plant elemental contents in Stagnosol.

significant biochar × fertilization interaction on N_2O emission was observed after harvesting in both the years. The N_2O emission after harvesting in both years were mostly low and often negative. The pairwise comparison showed that, after harvesting, biochar treatments had significantly higher N_2O emission in organic fertilization in 2017, and in mineral fertilization in 2018.

For CH_4 emission, the biochar × fertilization interaction was significant in Umbrisol on 2018-05-24, where biochar treatment with mineral fertilization reduced the soil CH_4 uptake (sink) compared to the corresponding mineral fertilization without biochar. A similar yet non-significant result was observed on 2018-09-08. The similar trend was also observed after harvesting in 2017 but only in case of organic fertilization ($p < 0.10$).

4. Discussion

4.1. Crop biomass yield increase by biochar as affected by fertilization and soil nutrient status

In this study, biochar additions increased crop biomass yield only in two cases during the eight years of our four long-term experiments on two different boreal soils. The result is in agreement with the meta-analyses (Jeffery et al., 2017; Liu et al., 2019; Ye et al., 2020), which showed that yield increases by biochar are more pertinent to tropical and sub-tropical regions. The short-term benefit of biochar in crop yield results from liming effect of biochar and direct addition of nutrients contained in soil, which will eventually decrease with time (Ye et al., 2020). Whereas in long-term, improvement of soil physical properties enhancing the nutrient and water holding capacity of soils (Kätterer et al. 2019; Liu et al., 2019; Zhang et al., 2020b), and increased CEC with

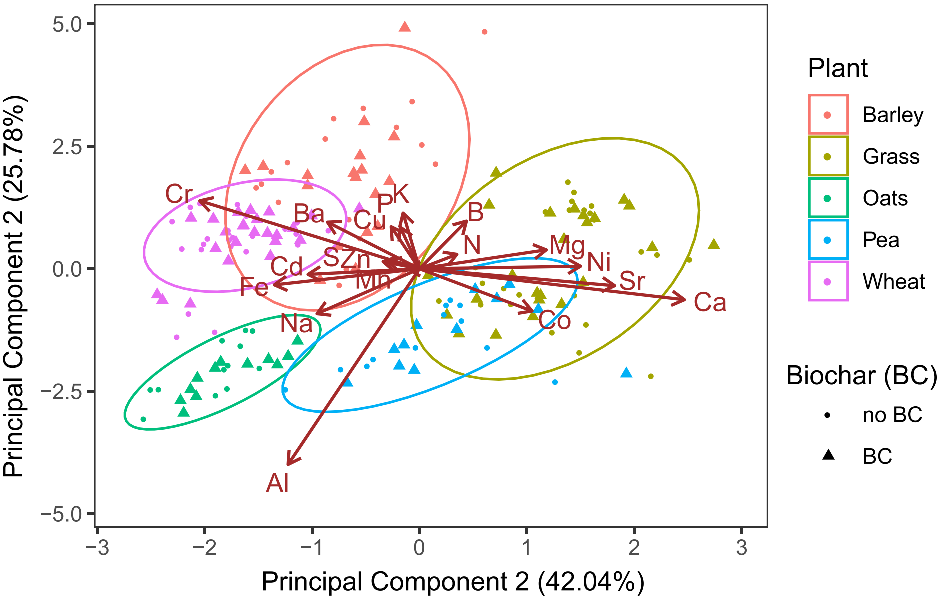


Fig. 7. Principal Component Analysis of plant elemental contents in Umbrisol.

the surface oxidation of biochar (Cheng et al., 2006; Mia et al., 2017a) can be the reasons for the positive effect of biochar. However, such short and long-term effects are probably not significantly relevant to the organic-rich and nearly neutral boreal soils.

It is easy to understand that increases in crop productivity by biochar will be evident only when the application of the biochar ameliorates the constraints in growth factors that limit the crop productivity (Laird et al., 2017). The two cases when biochar significantly increased crop biomass yield at the higher fertilization rate in Stagnosol can be attributed to the higher supply of nutrients, especially N and P. In general, biochar rarely improved the plant uptake of both N and P except for in these two cases. The plant contents of N and P by peas in 2016 were also increased by biochar at the higher fertilization rate. Such enhanced N and P supply by biochar can be linked to the pre-crop effect. In both cases, the fields were sown with N-fixing legume in the preceding growing season (faba bean in 2012 before barley, and red clover in 2014–2015 before peas). The N-fixing legumes can increase the supply of N available to the crop in the succeeding growing season (Bruulsema and Christie, 1987; Peoples et al., 2009), and the mobilization of fixed P in soil through the secretion of organic acids (Richardson et al., 2009; Shen et al., 2011). Moreover, some biochars have potential to enhance biological nitrogen fixation in legumes (Rondon et al., 2007). Thus, biochar could have promoted and retained N resulted from the N-fixation during the previous growing seasons, and also with peas in 2016. Moreover, the early growing season in May 2016 was extremely dry (Fig. B.1). The higher crop biomass of peas by biochar at that time could also be the result of increased seedling resistance to wilting by biochar (Mulcahy et al., 2013).

In Umbrisol, fertilization expectedly increased crop biomass yields in all growing seasons, when fertilizers were applied, except for in 2016 (barley) and 2017 (peas). The exceptions are attributed to the disease infection in 2016 and the relatively low rate of recommended N fertilizer application in 2017 (Table A.3) because of capability of peas to fix N. The effect of fertilization was also comparatively lower in 2018 than in the earlier growing seasons, likely because it was a comparatively drier and hotter growing season. In Stagnosol, the biomass yields of wheat and barley were consistently higher with the higher fertilization rate, as expected, because the fertilizer requirements (especially N) for wheat and barley are comparatively higher than for legumes (Viljavuuspalvelu Oy, 2000).

4.2. Plant uptake of elements as affected by biochar, fertilization and soil nutrient status

We observed that during the first year of biochar application, biochar decreased the nutrient contents in plant biomass in Stagnosol (Table C.3), although no effect on crop biomass yield was observed. Initially, biochar usually contains labile carbon that can stimulate microbial growth right after application (Bruun et al., 2012), and incorporation (immobilization) of the nutrients into microbial biomass might limit the amount and supply of available nutrients to the plants. In addition, because of negative surface charge, the fresh biochar can adsorb cationic nutrients (Yao et al., 2012). Such adsorbed nutrients may not be fully available for the plants and this may sometimes negatively affect the plant growth (Kammann et al., 2015). Similarly, Llovet et al. (2021) observed that fresh biochar reduced NO_3^-, Cl^-, Na^+, Ca^{2+} and Mg^{2+} concentrations in soil solution. They concluded that the possible mechanisms such as sorption, leaching, microbial immobilization, volatilization, plant uptake, and ecotoxicological effects could not explain the reason behind this result. So, they hypothesized the potential mechanism to be the trapping of nutrient-rich water in fresh biochar pores as enhanced by the formation of organo-mineral coating.

The most noticeable effect of biochar observed was the increased plant K content, especially in Umbrisol. This is consistent with the literature (Biederman and Harpole, 2013; Gaskin et al., 2010; Oram et al., 2014). Since K might not have been the most limiting factor affecting the plant growth, even in the nutrient deficient Umbrisol, its enhancement in crop biomass with biochar was unable to increase crop biomass yield. Higher plant content and uptake of K in 2014 and 2015, when no fertilizer was applied, reflects the long-lasting K fertilization effect of biochar. The application of 30 Mg ha^{-1} of biochar added 136 kg ha^{-1} total K in the soil, most of which is in the plant available form (Ippolito et al., 2015), that resulted in significant increase in soil K availability in the early years (Tammeorg et al., 2014b).

Even though no consistent effect of biochar was observed on N uptake, biochar increased NUE over the period of eight years since application especially when applied with mineral fertilization in Umbrisol. The application of biochar can reduce the loss of added N fertilizer as N_2O emission and N leaching (Borchard et al., 2019; Kalu et al., 2021; Liu et al., 2019) enhancing further the supply of N to plants. Similarly, biochar can also reduce K leaching (Kuo et al., 2020), increasing the

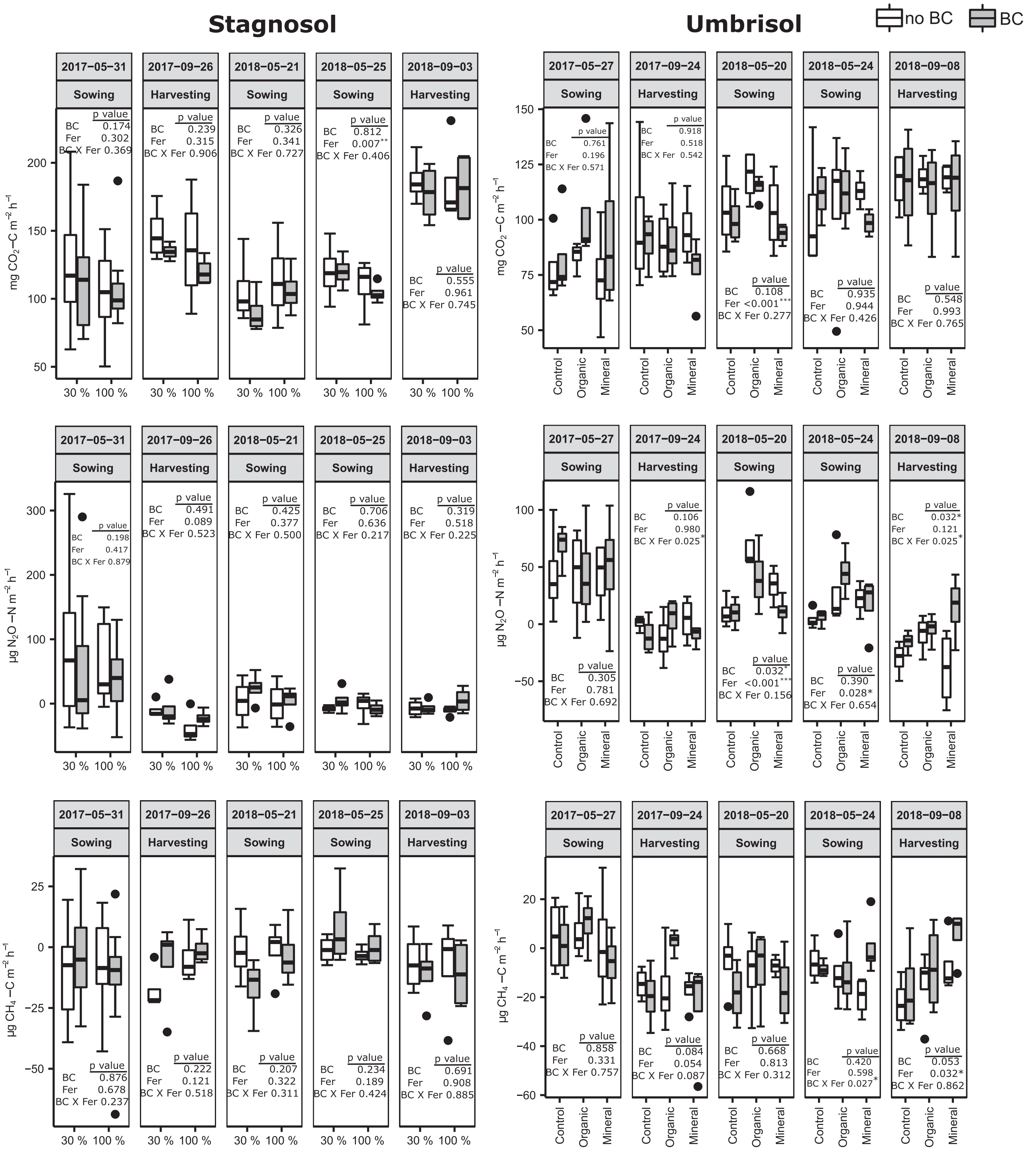


Fig. 8. The fluxes of CO_2, N_2O and CH_4 measured from the different fertilizer treatments (Fer) without or with added biochar (BC) as well as the statistical significance of experimental factors in the Stagnosol and Umbrisol fields in 2017 and 2018 after sowing and harvesting. The information about the box and whiskers is same as in Fig. 1.

availability of added mineral K fertilizer to plants and hence promoting higher KUE. Furthermore, biochar can convert slowly available-K to available K by stimulating K-dissolving bacteria and changing composition of clay minerals (Wang et al., 2018; Zhang et al., 2020c).

The K:Mg ratio in biochar treatments with the mineral fertilization was consistently higher during most of the growing seasons compared to the mineral fertilization treatment without biochar in Umbrisol. This finding was further supported by the roughly opposite directions of the K and Mg vectors in the PCA plot. Biochar reduced the average Mg content and uptake in several cases, although the reduction was not statistically significant (seven out of eight cases for Mg concentration with one significant reduction, and five out of eight cases for Mg uptake). This indicates an antagonistic effect of K on Mg with biochar. A similar biochar stimulated antagonistic effect on the uptake of both Ca and Mg in maize was observed in a pot experiment (Bornø et al., 2019). However, such reduced Mg uptake as an effect of K antagonism did not affect the crop biomass yield.

Biochar distinctly reduced plant Na content and uptake in the

Stagnosol field. This effect has been previously reported for saline soils (Akhtar et al., 2015; Feng et al., 2018; Hammer et al., 2015). Biochar also increased the K:Na ratio in Stagnosol. Also, the vectors of K and Na were in opposite directions in the PCA plot, hence the reduced Na content and uptake may also be explained by the antagonistic effect of K. Glaser et al. (2015) reasoned that the reduced Na uptake observed in maize by biochar produced from miscanthus as an antagonistic effect of K. Similarly, biochar noticeably reduced plant Al content and uptake in Stagnosol. This was more evident with faba bean (observed in all three cases) during the early growing seasons. The plant availability of Al might have reduced because of fixing of Al ions in biochar surface through the complexation of Al with hydroxyl and carboxylic groups, and the surface electrostatic adsorption of Al (Qian and Chen, 2013). The increase in soil pH after biochar addition can reduce the plant availability of Al (Hale et al., 2020). However, no effects of biochar on soil pH was observed in our study due to negligible liming efficacy of these softwood biochars (Tammeorg et al., 2014a, 2014b).

4.3. *Temporal effects of biochar on plant biomass yield and elemental uptake*

The regression lines of the average normalized value for AGB and for most of the macro-nutrient contents in plant biomass were almost always greater than 1 in Umbrisol, which indicate the prevalence of increased fertility effects by biochar. This is most likely because of sandy soil and higher rate of biochar application compared to Stagnosol. Nevertheless, due to the high variance, the uncertainty is large. However, the slopes of the normalized value lines were not different from zero for AGB and plant macro-nutrient contents indicating that the biochar effect did not change them significantly over the time in Umbrisol. On the other hand, biochar increased the plant Cd and Ni content while decreased plant Mn content over the years. Similar to our results, Abbas et al. (2017) also reported that right after biochar addition decreased the contents of Cd and Ni, and increased that of Mn in wheat. The Mn present in the biochar could be easily accessible for plants, but it might have depleted over years. On the other hand, added biochar may also form biochar-metal ion complexes or chelates (Lin et al., 2012). Depending on the water solubility of such chelates, the plant availability of metal ions may increase or decrease. Moreover, Graber et al. (2014) claimed that water extractable organic compounds from biochar increased the solubility of Mn because of reduction. It is well known that fresh biochars contain variable amounts of relatively easily decomposable "volatile fraction", which is more likely responsible for such chelating and reduction effect. Such semi-stable fractions could play an important role in determining any transient effects during the first years after biochar application.

The changes in biochar particles due to field aging could be responsible for increased plant nutrient contents over the year. The field aging increase more oxygen containing functional groups such as carboxylic and phenolic groups in the surfaces of biochar, which further enhance negative surface charge density and CEC of biochar (Cheng et al., 2006; Mia et al., 2017a). As a result, the plant availability of the cationic nutrients (especially fertilizer applied every year) could have increased over the years because of increased electrostatic adsorption of such nutrients in deprotonated carboxylic and phenolic groups in the biochar's surface. In principle, the adsorption of anionic species, such as $H_2PO_4^-$ and SO_4^{2-}, is expected to decrease as biochar ages because of more negative surface charge. However, the aging of biochar can release a range of organic compounds. These compounds can increase the adsorption of anionic species too, increasing their retention in soil and uptake by plants as biochar ages (Mia et al., 2017c).

The increased plant nutrient content over time by biochar could also be due to the initial incorporation or immobilization because of sorption of the nutrients present in soil into biochar surfaces or pores, which becomes plant available as the biochar weathered in the soil. During the first year after biochar application, the average normalized values for Cd and Ni content were always lower than 1 but increased over due course of time. This suggests that right after application, biochar could have fixed the Cd and Ni present in soil by adsorbing into its surfaces, but more of those elements became plant available as biochar aged. Moreover, as biochar itself added a fair amount of K, Mg, P, S, Al, Cu, Fe and Ni (Table A.6) to soil, the weathering of biochar particles might have made these elements in biochar particles soluble, which became plant available as biochar aged in the field. The supply of the initially fixed Al by biochar and/or Al present in biochar over time may explain the significant reduction only during the initial growing seasons with biochar in Stagnosol. However, the average Al content in biochar treatment was lower compared to no biochar treatment for later growing seasons as well.

The changes in biochar properties over time have been reported for enhanced retention of mineral N – increased ammonium retention in cation exchange sites (Mia et al., 2017b) and increased nitrate retention in biochar pores aided by the development of organic coatings in the pores (Hagemann et al., 2017; Joseph et al., 2018). However, no temporal effects of biochar on N content in plants were observed. Field-aged biochar has been reported to have a higher tendency to retain/capture nitrate ions than ammonium, however, those nitrate ions are not easily extractable (Haider et al., 2016) suggesting that such nitrate diffused in small biochar pores might not be easily accessible for plant uptake.

4.4. *Effects of biochar on soil physical properties and greenhouse gas emissions*

The GHG fluxes were measured only after sowing and harvesting in 2017 and 2018, at times when the N_2O emissions could generally be expected to be high. Due to temporally sparse sampling, our data thus does not allow the estimation of biochar effects on cumulative GHG emissions as the effects were tested only in a limited number of environmental conditions and we might have failed to capture the peak emission periods. Nevertheless, this does not invalidate the few significant results on the long-term biochar effects on GHG emissions in this study. Most notably, about a one-third reduction of N_2O emissions by biochar treatments in one of the measurement periods in spring 2018 in Umbrisol agrees with the range of the average N_2O emission reduction by biochar reported in recent meta-analyses (Borchard et al., 2019; He et al., 2017; Zhang et al., 2020a). The trapped nitrate ions inside the pores of field-aged biochar might not be accessible for denitrification (Haider et al., 2016). Also, the field-aged biochars have been reported to significantly suppress autotrophic nitrification (Fan et al., 2020; Liao et al., 2021), and nitrifier- denitrification and heterotrophic- denitrification (Zhang et al., 2021) thereby reducing N_2O emissions. On the other hand, we also observed that, after harvesting, the N_2O fluxes were generally low and biochar had a few significant but inconsistently increasing effects on them depending on the fertilizer and year. This might be because of the carboxylic functional group on the field-aged biochar surfaces that can inhibit N_2O reduction by hampering the supply of electrons to N_2O-reducing microbes (Yuan et al., 2021). In addition, Duan et al. (2018) reported that field-aged biochar can increase N_2O emissions via both nitrification and denitrification processes. This controversial effect of field-aged biochar on N_2O emissions calls for further research on the topic to reveal the involved mechanisms.

We observed the interaction of biochar and N fertilization effect on CH_4 flux. Jeffery et al. (2016) demarcated the threshold that when a biochar is applied with a N fertilizer at the rate below 120 kg N ha^{-1}, the biochar increase sink strength or decrease source strength of CH_4, while above that threshold, there is no effect. Such an increase in sink strength with higher N fertilization is linked to the fact that adding ammonium fertilizers into soil tend to increase the microbial ammonium oxidizers in soil. Methanotrophs can also oxidize ammonium besides methane (Nyerges and Stein, 2009). Even if increased availability of ammonium increases the growth and activity of ammonium oxidizers and methanotrophs, NH_4^+ is preferentially oxidized relative to CH_4 by the law of mass action (Dunfield and Knowles, 1995). Accordingly, this should result in less oxidation of CH_4 with increased NH_4^+-N availability. The increased source strength of CH_4 in our study from the biochar treatment with mineral fertilizer denotes that biochar could have enhanced the availability of NH_4^+-N to the methanotrophs, consequently inhibiting the CH_4 oxidation compared to the mineral fertilizer treatment without biochar.

During the initial years of biochar application, some effects of biochar were observed on soil physical properties especially in the coarse textured Umbrisol. These include decreased bulk density, increased porosity and increased AWC (Tammeorg et al., 2014b). However, such effects disappeared after seven growing seasons following the biochar application. The effectiveness of biochar on influencing GHG flux indicates that considerable amount of biochar still persisted in the field, even after seven growing seasons, while the disappearance of biochar-induced effects on soil physical properties on top-soil suggests downward movement of biochar. The degradation of soil structure in topsoil due to continuous tilling might have also contributed in the fading of initially observed changes in soil physical properties due to biochar addition.

5. Conclusion

In our long-term field experiment on two boreal soils with contrasting fertility status, we found generally little effects by softwood biochar additions on crop biomass yield. Notably, some exceptional positive cases were observed in which the increased crop biomass yields were associated with an enhanced N and P supply or linked to the pre-crop effect of N-fixing legumes in the previous year. Such possible synergies of enhanced N-fixation and biochar addition in certain combinations with pre-crops warrant further studies.

The most noticeable effects by biochar additions were the increased plant K content in the nutrient deficient Umbrisol, as well as the decrease in content and uptake of Al and Na in the fertile Stagnosol. These findings suggest that biochars can function as a K source in K poor soils and may relieve the salinity and aluminum toxicity stress of plants. The added biochar enhanced the plant availability of Mn in Umbrisol right after biochar application probably due to plant availability of Mn present in biochar or increased solubility of soil-Mn by biochar, but the availability decreased over the years. On the other hand, softwood biochar increased the plant availability of some other elements like K, P, Mg, S, Al, Cd, Cu, Fe and Ni over the years. Such increased plant availability over the years could be the result of increased sorption of elements because of increased CEC due to surface modification of the biochar particles, release of these elements from the biochar particle itself because of field aging, and initial fixation of these elements present in soil into the biochar's surface, which later became plant available as the biochar weathered in the field. In addition, the initial beneficial effects of biochar on soil physical properties and increased plant available water became weaker over time, likely due to the downward movement of biochar in the soil profile. The effects of biochar on N_2O emissions in the long-term needs to be further explored with more frequent measurements along with mechanistic study. In addition, studying the properties of the field-aged biochar particles and comparing that with archived fresh biochar would facilitate in understanding the underlying mechanism.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors gratefully acknowledge funding from several Finnish funding bodies without which this long-term study would have been impossible. We thank The Ministry of Agriculture and Forestry of Finland, University of Helsinki Three-Years' Grant (Decision number HY/66/05.01.07/2017), University of Helsinki HiLIFE Fellows funding, Jenny and Antti Wihuri Foundation, The Finnish Cultural Foundation, Niemi Foundation, Maj and Tor Nessling Foundation, Emil Aaltonen Foundation, OLVI Foundation, August Johannes and Aino Tiura Agricultural Research Foundation and the Future Fund of University of Helsinki. We also thank laboratory technician Miia Collander for the technical support in the lab, Pierre Boivin for assisting with Umbrisol sample analysis, as well as Jure Zrim for helping with GHG measurement with Gasmet.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.agee.2021.107454.

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