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# Addition of softwood biochar did not reduce $N_2O$ emissions or N leaching from peat soil in the short term

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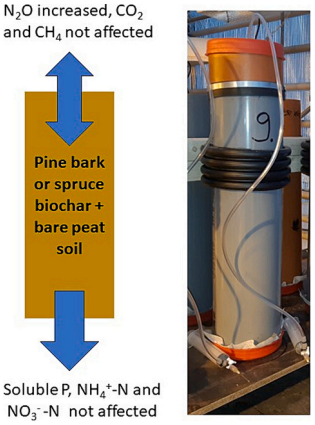
## HIGHLIGHTS

- Low application of pine bark biochars increased $N_2O$ efflux in peat soil at first.
- Biochar application did not affect $CO_2$ and $CH_4$ fluxes in peat soil.
- Biochar application did not affect nutrient leaching from peat monoliths.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Drained agricultural peat soils pollute both the atmosphere and watercourses. Biochar has been observed to decrease greenhouse gas (GHG) emissions and nutrient loading in mineral soils. We studied effects of three biochar types with two application rates (10 and 30 Mg $ha^{-1}$) on GHG fluxes as well as N and P leaching on peat soil. Peat monoliths were drilled from a long-term cultivated field and were watered either slightly (five dry periods) or heavily (four rainfall periods) during an 11-month laboratory experiment with intact peat columns. The incubation of bare peat profiles enhanced peat decomposition leading to high $CO_2$ (up to 1300 mg $CO_2$ $m^{-2}$ $h^{-1}$) and $N_2O$ emissions (even 10,000–50,000 μg $N_2O$ $m^{-2}$ $h^{-1}$) and $NO_3^-$-N leaching (even 300–700 mg $L^{-1}$) in all treatments. In the beginning of the experiment, the lower application rate of pine bark biochars increased $N_2O$ emission compared to control, but otherwise none of the biochars or their application rates significantly affected gas fluxes or nutrient leaching. These results indicate that moderate softwood biochar application does not help to mitigate the environmental problems of agricultural peat soils. Higher application rate of biochar pyrolyzed at high temperature is recommended for further studies with peat soils.

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## 1. Introduction

The overall area of peatlands in Europe is approximately 594 $km^2$, and globally 4.23 million $km^2$, which corresponds to about 2.8 % of the world land area (Tanneberger et al., 2017). Despite their small coverage, peatlands are major global carbon (C) and nitrogen (N) reservoirs. Presumably, 63 million hectares of peatland are drained for different human purposes (Joosten and Couwenberg, 2009). Drying of peat soils eliminates methane ($CH_4$) emissions, but carbon dioxide ($CO_2$) and nitrous oxide ($N_2O$) emissions increase due to the increased rate of peat decomposition. Agricultural activities such as liming, fertilization and ploughing enhance microbiological activity further increasing $CO_2$ and $N_2O$ production leading to emissions of up to 10 to 100 t $CO_2$-eq. per hectare per year (Joosten and Couwenberg, 2009). The increased decomposition of peat after drainage also increases the leaching of nutrients such as N and phosphorus (P) (Laiho and Laine, 1994). Although part of the N and P released during the enhanced decomposition of peat is taken up by plants, immobilized by microbes and retained chemically in soil, significant amounts of N and P are also released from drained peatlands to water resources (e.g. Nieminen et al., 2017; Pham et al., 2023). To achieve carbon neutrality and nutrient retention targets in the agricultural sector, effective ways to reduce greenhouse gas (GHG) emissions and nutrient leaching from drained cultivated peat soils are needed. One possible but little researched way to reduce environmental disadvantages from cultivated peatlands could be biochar amendments.

The effects of biochar addition on GHG fluxes have been studied abundantly in mineral soils. Meta-analyses suggest that $CO_2$ emissions increase, $N_2O$ emissions decrease and $CH_4$ uptake decreases in drained agricultural soils after biochar treatment (Cayuela et al., 2014, Jeffery et al., 2016, He et al., 2017, Song et al., 2016). The effects are, however, not constant but depend on many factors, such as the source material and production temperature of the biochar or the pH and texture of the soil as well as the application rate and duration of the experiment. The same factors also affect nutrient leaching from the ecosystem, which is a complex process involving numerous biological, chemical and physical processes. According to earlier studies in mineral soils, the addition of biochar typically decreases N leaching but even increases or does not affect P leaching (Saarnio et al., 2018; Borchard et al., 2019; Saarnio and Kettunen, 2020; Almanassra et al., 2021; Lu et al., 2022). Again, the effects of biochar on leaching are not constant but depend on the properties of the biochar and soil as well as the biological processes, nutrient source, application rate and duration of the experiment (Borchard et al., 2019; Saarnio and Kettunen, 2020; Almanassra et al., 2021).

In this study, we examined the effects of different biochars and their application rates on $N_2O$ emissions, soil respiration, $CH_4$ uptake as well as N and P leaching using 60 cm deep peat profiles cored from an arable peat field cultivated for >140 years. Three different biochars, BSH (made from spruce at 600 °C), BPM (made from pine bark at 450 °C) and BPL (made from pine bark at 350 °C), were used at two application rates (10 and 30 Mg $ha^{-1}$). Several factors like slightly acidic soil (pH 5.5), source material (bark and wood) and thus high C:N ratio of our biochars (98–134) and no N fertilization support the hypothesis (1) that $N_2O$ emissions would be reduced also in this experiment (Cayuela et al., 2014; Borchard et al., 2019). The source material (bark and wood), pyrolysis temperature (350–600 °C), high biochar C:N ratio and the dry-wet cycle in the soil during the experiment are all factors supporting the hypothesis, that (2) net $CH_4$ uptake decreases due to biochar application (Jeffery et al., 2016; Ji et al., 2018). The hypothesis that (3) $CO_2$ release would increase (at least in the short-term) under biochar treatments is supported by the freshness of the biochar, the low pyrolysis temperatures (350 and 450 °C) and the lack of fertilization, which all indicate that labile compounds are available, and they decompose after biochar addition (Saarnio, 2016; He et al., 2017). The slightly acidic soil, high C:N ratio of biochars and high production temperature (600 °C) supported the hypothesis that (4) N leaching would decrease from biochar (at least spruce biochar) treated columns (Borchard et al., 2019; Saarnio and Kettunen, 2020). As the biochars used were unmodified and not rich in metal elements, (5) they were not hypothesized to affect P leaching (Yin et al., 2019; Almanassra et al., 2021).

## 2. Materials and methods

### 2.1. Properties of the soil and biochars

The undisturbed peat profiles (600 mm) for this study were cored into polyvinyl chloride tubes (Ø 160 mm) from a peat field in Jokioinen, Finland (60.22°N, 24.78°E) in November 2018. The depth of the peat layer at the sampling point was >60 cm, and it ranged from 0.8 to 2 m in the plot. The field has been conventionally cultivated, tilled, and used for cereal and grass cultivation for >140 years. The N fertilization level has been varied from 60 to 100 kg $ha^{-1}$ during the crop rotation. The crop preceding the time of soil sampling was oat (*Avena sativa*).

Soil properties were examined at the beginning and at the end of the experiment (Table 1). At the beginning of the experiment, 16 subsamples representing the whole field plot were taken from the topsoil (0–20 cm) in May 2018 and the average results are presented. At the end of the experiment, soil samples were taken from each monolith and thus they also included the applied biochar. The samples were sent to the laboratory of Eurofins Finland for analyses of pH, Ca, P, K, Mg and S contents (mg $L^{-1}$ soil) and electrical conductivity (EC, 10 x mS $cm^{-1}$). Cation exchange capacity (CEC, cmol $kg^{-1}$) was analyzed by Eurofins at the end of the experiment but at the beginning of the experiment we used a CEC calculator created by Mattila and Rajala (2018). The soil C and N contents were determined in samples taken in May 2018 from the 0–20, 20–40 and 40–60 cm layers using the dry combustion method (Leco TruMac CN Determinator, Leco Corp. St. Joseph, MI, USA). The C content was 250, 300 and 320 mg $g^{-1}$ and the N content was 14, 16 and 18 mg $g^{-1}$ in the air-dried samples of the studied layers, respectively.

Two of the biochars (BPL and BPM) were manufactured in the pyrolysis facility at the Natural Resources Institute in Jokioinen, Finland. The material used for BPL and BPM was pine (*Pinus sylvestris*) bark originating from a sawmill. The bark mass was separated from the other wood material by hand and cut into particles of about two centimetres which were pre-dried in an oven at 40 °C for over four days before pyrolysis. The slow pyrolysis device was a bench-scale batch-type pyrolysis oven with an external electric heating system (Hyväluoma et al., 2018). The process was made completely oxygen-free by checking the adhesion of the joints prior to pyrolysis and by running nitrogen gas ($N_2$) through the system. One of the pine bark biochars (BPL) was pyrolyzed at 350 °C and the other one (BPM) at 450 °C. The third biochar (BSH) was a commercially available product of Carbofex Oy (Carbofex Biochar) made of spruce (*Picea abies*) wood and pyrolyzed approximately at 600 °C.

The biochar samples were ground and sieved (2 mm) for the laboratory analyses and their properties were assayed in triplicate (Table 2). The electrical conductivity (SFS-EN 27888) and pH (ISO 10390:2005) were determined in a 1:5 water solution, and the ash content was obtained from the loss of ignition (SFS-EN 13039). P was determined from aqua regia extract using an ICP instrument (ISO 11885). Elemental contents were determined with the dry combustion method (Leco TruMac CN Determinator, Leco Corp. St. Joseph, MI, USA). The specific surface area and pore size distributions of both pine bark biochars were determined by the Brunauer-Emmett-Teller (BET) analysis with $N_2$ sorption analysis at 77 K with a surface analyzer (TriStar II 3020 Micromeritics Instrument Corporation, USA) after degassing at 300 °C. However, the pores of both pine bark biochars were filled with pyrolysis oil and thus the temperature of the BET analysis could not be raised to high enough to achieve proper analysis as the oil would have stained the machine badly. Information on the surface and porosity properties of the spruce biochar was provided by the manufacturer.

The water holding capacity (WHC) of the biochars and peat soil

mixed with biochar taken from each treatment after the experiment were determined from samples (fresh-weight) of 5 g for biochar and 10 g for biochar + soil. The samples were dried overnight at 105 °C and weighed (Wsd), and the dried samples were placed in a stoppered funnel with moistened and weighed (Wfm) filter paper. The samples were soaked in 50 ml of sterile water placed on top of the samples for over 2 h and then the funnels were opened, and the excess water was allowed to drain for 1 h. The filter paper with the samples was weighed (Wsm). The WHC (g water $g^{-1}$ soil) was calculated as a quotient: (Wsm − Wfm − Wsd)/Wsd.

### 2.2. Experimental setup

Three different biochars with two different application rates (10 and 30 Mg $ha^{-1}$) were mixed to the surface layer of randomly selected monoliths down to the depth of about 15 cm in order to represent tilling after the spreading of biochar. The soil in the control monoliths was also mixed to the same depth. There were four replicates in each of the seven treatments.

Peat profiles were stored for 35 days in a greenhouse where they were kept field moist until the start of the experiment by adding water as needed to maintain the original weight. The temperature in the greenhouse was ca. 22 °C during April–September and approx. 15 °C during the wintertime. Monoliths were watered regularly throughout the experiment. Monoliths were placed in racks where their places were changed once a month. All germinating vegetation was removed.

### 2.3. Greenhouse gas sampling and analysis

GHG emission measurements were started next day after the biochar additions. Fluxes of $CH_4$, $CO_2$ and $N_2O$ were measured 53 times during 11 months. For gas sampling, the peat monoliths were closed with a 2010 $cm^3$ opaque chamber sealed with a rubber seal and a hose clamp. The total volume of the chamber and airspace above the peat was approximately 6900 $cm^3$. Three 20 ml gas samples were taken 0, 10 and 20 min after the chamber closure using a plastic syringe with a needle. The samples were stored in pre-evacuated vials (Exetainer, Labco Ltd., High Wycombe, UK) and analyzed using a gas chromatograph equipped with electron capture and flame ionization detectors and a nickel catalyst for converting $CO_2$ to $CH_4$ (HP 7890 Series, GC System, Hewlett Packard, USA). The gas flux rate was determined from the linear change of the gas concentration in the chamber during the 20 min enclosure.

### 2.4. Rainfall treatments and water sampling

To assess the effect of the biochars on nutrient leaching we simulated heavy rainfall four times during the experiment. The first rainfall treatment was given on 1th–5th April, second 6th–10th May, third 9th–13th September and fourth 26th–27th September. During the rainfall treatments, the daily amount of given water was 531 ml (5 days), 354 ml (5 days), 354 ml (5 days) and 354 ml (2 days), respectively. The amount was given with a syringe as a single dose. The water used was tap water which contained 0.065 mg $NH_4^+$-N $L^{-1}$ and 6.1 mg $NO_3^-$N $L^{-1}$ but not a measurable amount of soluble phosphorus. The excess water percolated through the peat monoliths and dropped via a filter cloth covered hole (Ø 40 mm) from the bottom plug to containers placed underneath.

The volume of water percolated through the soil columns was measured once a day, and a 50 ml sample of that water was taken for nitrate nitrogen ($NO_3^-$N), ammonium nitrogen ($NH_4^+$-N) and soluble phosphorus ($PO_4^-$P) analyses. The rates of $CH_4$, $CO_2$ and $N_2O$ gas fluxes between the soil and the atmosphere were measured daily during the rainfall periods and twice during the first week after the rainfall treatments.

The total amounts of $NO_3^-$N, $NH_4^+$-N and $PO_4^-$P (mg) leached from the peat monoliths during each rainfall event were calculated by multiplying the concentrations (mg $L^{-1}$) by the leached water amount (L) and the daily values were summarized for one value per rainfall event. These cumulative amounts were used in the statistical analyses.

### 2.5. Statistical analyses

Both gas flux, nutrient leaching and soil data was analyzed using generalized linear mixed model (GLMM) by using GLIMMIX procedure in SAS Enterprise Guide 7.1 (64-bit) software. Degrees of freedom we calculated using the Kenward-Roger method and multiple comparisons between treatments were tested using Tukey-Kramer method. Methane fluxes, leached soluble P, WHC, Ca, P, K, Mg, S, EC, CEC and pH of the soil were assumed to follow normal distributions, while $CO_2$ and $N_2O$ fluxes were assumed to follow gamma distributions. The leached $NN_4^+$

**Table 1**
Soil properties at the beginning and at the end of experiment (mean ± standard deviation, $n = 4$ in each treatment). Values have been calculated from the original data whereas the different letters within columns are based on generalized linear mixed models (Table 4) and indicate statistically significant difference at $\alpha = 0.05$.

| Treatment | pH[a] | Soil sample with biochar, water holding capacity g water $g^{-1}$ soil | Calcium mg/l | Phosphorus mg/l | Potassium mg/l | Magnesium mg/l | Sulphur mg/l | Electrical conductivity 10 × mS/cm | Cation exchange capacity cmol/kg |
|---|---|---|---|---|---|---|---|---|---|
| At the beginning of experiment | | | | | | | | | |
| Aggregated sample | 5.5 ± 0.1 | / | 3625 ± 326 | 4.4 ± 0.7 | 172 ± 35 | 260 ± 36 | 16.5 ± 0.9 | 1.40 ± 0.1 | 34* |
| At the end of experiment | | | | | | | | | |
| Control | 5.18 ± 0.05ab | 0.85 ± 0.08a | 3750 ± 129a | 4.05 ± 0.17a | 180 ± 8.16a | 278 ± 17.1a | 28.5 ± 2.38a | 5.15 ± 0.61a | 41 ± 1.41ab |
| BPL10 | 5.07 ± 0.13b | 0.73 ± 0.11a | 3525 ± 95.7a | 4.25 ± 0.57a | 175 ± 20.8a | 243 ± 22.2a | 28.8 ± 1.71a | 5.03 ± 0.59ab | 41.5 ± 2.89ab |
| BPM10 | 5.13 ± 0.05ab | 0.83 ± 0.20a | 3650 ± 129a | 3.93 ± 0.21a | 175 ± 25.2a | 273 ± 17.1a | 26.5 ± 1.29a | 4.80 ± 0.51ab | 41 ± 0.82ab |
| BSH10 | 5.08 ± 0.10b | 0.83 ± 0.20a | 3650 ± 300a | 4.53 ± 0.49a | 193 ± 29.9a | 273 ± 15a | 29.8 ± 1.71a | 5.23 ± 0.26a | 42.8 ± 1.26a |
| BPL30 | 5.08 ± 0.10b | 0.66 ± 0.16a | 3575 ± 206a | 4.2 ± 0.90a | 180 ± 18.3a | 268 ± 17.1a | 27.5 ± 0.58a | 4.83 ± 0.33ab | 41.8 ± 2.5ab |
| BPM30 | 5.20 ± 0.8ab | 0.84 ± 0.11a | 3550 ± 238a | 4.25 ± 0.52a | 183 ± 17.1a | 265 ± 17.3a | 26.8 ± 1.5a | 4.43 ± 0.05ab | 38.5 ± 1.73b |
| BSH30 | 5.25 ± 0.1a | 0.96 ± 0.07a | 3725 ± 532a | 4.43 ± 0.17a | 203 ± 15a | 273 ± 20.6a | 27.5 ± 1.0a | 4.10 ± 0.08b | 38.8 ± 2.5ab |

[a] Logarithmic value.
* value comes from CEC calculator (Mattila and Rajala, 2018).

**Table 2**
Properties of the biochars (mean ± standard deviation; see deviations from this in the footnotes).

| Biochar | Material | Pyrolysis temperature °C | Electrical conductivity μS/cm | Dry matter % | pH[a] | ash % | P g/kg dry matter | C % per dry matter | H % per dry matter | N % per dry matter | S % per dry matter | O % per dry matter | Specific surface area $m^2/g$[b] | Pore volume $cm^3/g$[b] | Water holding capacity g water $g^{-1}$ soil[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BSH | Spruce | 600 | 109 ± 12 | 96.1 ± 0.02 | 8.3 ± 0.11 | 2.7 ± 0.02 | 0.17 ± 0.003 | 92 ± 0.1 | 1.9 ± 0.04 | 0.69 ± 0.01 | 0.01 ± 0.00 | 2.6 ± 0.1 | 550,00 | NA | 1–1.7 |
| BPL | Pine bark | 350 | 86.4 ± 1.4 | 97.0 ± 0.05 | 7.8 ± 0.04 | 14 ± 1.6 | 0.76 ± 0.02 | 65 ± 1.0 | 3.8 ± 0.05 | 0.67 ± 0.01 | 0.03 ± 0.00 | 16 ± 1.6 | 1.01* | 0.0003 | 0.9–2.1 |
| BPM | Pine bark | 450 | 110 ± 4.2 | 96.9 ± 0.03 | 9.1 ± 0.02 | 13 ± 1.1 | 0.74 ± 0.02 | 74 ± 0.4 | 3.0 ± 0.03 | 0.7 ± 0.01 | 0.03 ± 0.00 | 8.9 ± 1.5 | 2.42* | 0.0057 | 2.2–2.7 |

NA = not available.
[a] Logarithmic value.
[b] No replicates.
[c] Only two replicates, range shown.
* Small values indicate that pores were filled with pyrolysis oil.

and $NO_3^-$ were assumed to follow log-normal distributions. Unequal variances were allowed for the treatments in all models, based on a likelihood ratio test. The assumption of normality of residuals was checked using residual plots.

Gas fluxes of each period were examined separately and compared by sampling date, treatment and as their combined effect, which were used as fixed effects. Time within a monolith was used as a R-side random effect having homogeneous or heterogeneous compound symmetry (CS and CS*H*) or unstructured (Un*r*) covariance structure within measurements from the same monoliths. The Akaike information criterion (AIC) was used to select the most suitable covariance structure.

## 3. Results

### 3.1. Gas fluxes

The $N_2O$ flux did not vary much between the measurements during the periods of steady moisture (Fig. 1). The first two rainfall events caused a clear peak in the flux rate but during the latter rainfall events only slight changes were observed. The rate of $N_2O$ flux differed significantly between the treatments only during the first dry period (D1), but differences between measuring dates were significant during almost all periods (Table 3). On the basis of the average $N_2O$ flux rate estimates for D1, treatment BPL10 differed from the control, BPL30, BPH30 and BSH10 treatments. Treatment BPM10 differed from the control and treatment BPL30.

The soil respiration rate followed the indoor air temperature, and there were small peak events during the rainfall periods (Fig. 2). The soil respiration rate differed significantly between the measurement dates during each period (Table 3). In addition, the interaction of date and treatment was significant during the first dry period (D1).

The methane flux differed significantly between the measurement dates during the two dry periods (D3 and D4) and the interaction of date and treatment was significant during the first dry period (D1) (Table 3).

### 3.2. Nutrient leaching

The total amount of ammonium, nitrate or phosphate (mg) in the percolated water and the total amount of percolated water (ml) differed significantly between the rainfall periods, but did not differ between the biochar treatments (Table 4). The monoliths behaved differently leading to high variation in the timing of leaching and amount of leaching within the events and within the treatments (Figs. 3, 4, Fig. S2).

### 3.3. Soil properties

Cation exchange capacity was statistically significantly higher in BSH10 treatment than in BPM30 treatment (Tables 1 and 4). The pH of the topsoil samples differed significantly between treatments BSH30 (highest) and BPL10, BSH10 and BPL30 (lowest). Electrical conductivity in BSH30 treatment was significantly lower than in control and BSH10 treatments. Despite the different source materials and production temperatures, water holding capacity of the pure biochars and topsoil samples did not differ significantly between the treatments.

## 4. Discussion

### 4.1. Nitrous oxide

During the first dry period, $N_2O$ emissions were low (<500 μg $m^{-2}$ $h^{-1}$), but they increased when the monoliths were drying after the heavy watering (some thousands μg $m^{-2}$ $h^{-1}$). Especially high emissions (even 10,000–50,000 μg $N_2O$ $m^{-2}$ $h^{-1}$) were recorded in all treatments after the watering done during the warmest period of the summer. The emission peaks were high compared to typical emissions measured in boreal peat fields (e.g. Maljanen et al., 2003a; Gerin et al., 2023), but not

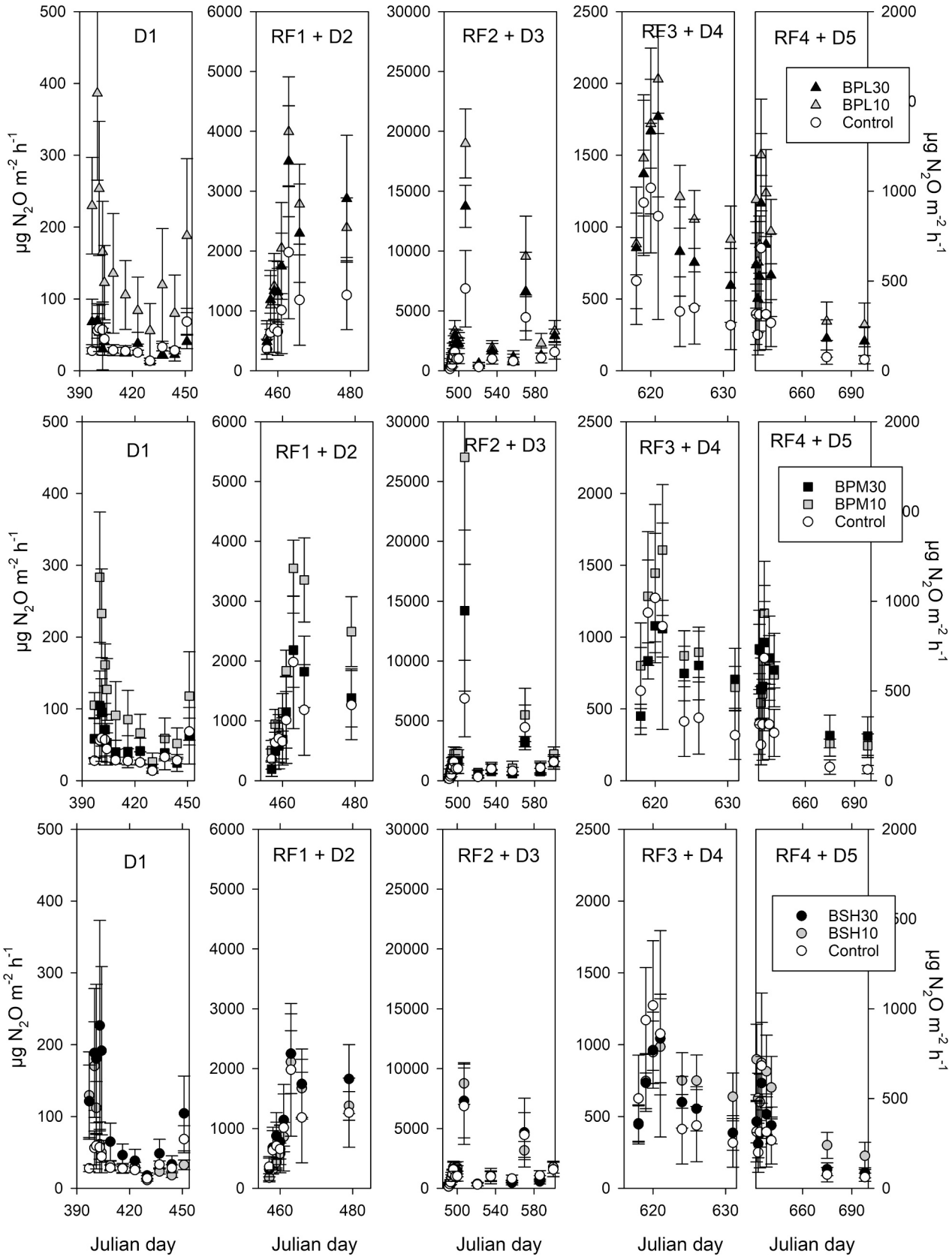


**Fig. 1.** Average (± standard error of mean) $N_2O$ flux in measuring days during dry periods (D1–D5) and rainfall events (RF1–RF4). Note the different scales between periods.

**Table 3**
Generalized linear mixed model results of $N_2O$, $CO_2$ and $CH_4$ fluxes for five dry periods (D1–D5) and four rainfall events (RF1–RF4).

| Season | Dates | Effect | $N_2O$-N g/ha/d | | | | $CO_2$-C g/ha/d | | | | $CH_4$-C g/ha/d | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Num DF | Den DF | F Value | Pr > F | Num DF | Den DF | F Value | Pr > F | Num DF | Den DF | F Value | Pr > F |
| D1 | 21.12.2018–1.4.2019 | Treatment | 6 | 18.1 | 3.35 | 0.0214 | 6 | 17.97 | 1.18 | 0.3611 | 6 | 21 | 1.13 | 0.3804 |
| | | Date | 12 | 250 | 26.11 | <0.0001 | 12 | 251 | 25.22 | <0.0001 | 12 | 252 | 1.65 | 0.0781 |
| | | Treatment * date | 72 | 250 | 1,06 | 0.3711 | 72 | 251 | 1.48 | 0.0141 | 72 | 252 | 1.45 | 0.0188 |
| D2 | 9.4.2019–5.5.2019 | Treatment | 6 | 18 | 1,68 | 0.1834 | 6 | 21 | 1.61 | 0.1943 | 6 | 21 | 0.83 | 0.5616 |
| | | Date | 1 | 21 | 0,62 | 0.4385 | 1 | 21 | 254.67 | <0.0001 | 1 | 21 | 1.14 | 0.2987 |
| | | Treatment * date | 6 | 21 | 0,75 | 0.6144 | 6 | 21 | 0.85 | 0.5489 | 6 | 21 | 1.28 | 0.3065 |
| D3 | 14.5.2019–9.9.2019 | Treatment | 6 | 18 | 1.64 | 0.1929 | 6 | 18 | 0.79 | 0.5872 | 6 | 18 | 0.33 | 0.9103 |
| | | Date | 8 | 147.3 | 127.21 | <0.0001 | 8 | 147.4 | 112.36 | <0.0001 | 8 | 148.9 | 5.66 | <0.0001 |
| | | Treatment * date | 42 | 147 | 0.90 | 0.6463 | 42 | 147 | 44,531 | 0.3002 | 42 | 147 | 0.86 | 0.7090 |
| D4 | 14.9.2019–25.9.2019 | Treatment | 6 | 18 | 1.34 | 0.2920 | 6 | 18 | 0.56 | 0.7532 | 6 | 21 | 1.66 | 0.1815 |
| | | Date | 2 | 42 | 25.59 | <0.0001 | 2 | 42 | 9.46 | 0.0004 | 2 | 42 | 4.56 | 0.0161 |
| | | Treatment * date | 12 | 42 | 0.99 | 0.4761 | 12 | 42 | 0.88 | 0.5710 | 12 | 42 | 1.00 | 0.4690 |
| D5 | 28.9.2019–29.11.2019 | Treatment | 6 | 18 | 1.99 | 0.1198 | 6 | 18 | 1.88 | 0.1393 | 6 | 18 | 0.97 | 0.4711 |
| | | Date | 3 | 63 | 201.34 | <0.0001 | 3 | 63 | 55.13 | <0.0001 | 3 | 63 | 0.30 | 0.8220 |
| | | Treatment * date | 18 | 63 | 0.69 | 0.8092 | 18 | 63 | 0.57 | 0.9072 | 18 | 63 | 0.70 | 0.7960 |
| RF1 | 2.4.2019–8.4.2019 | Treatment | 6 | 18.01 | 1.98 | 0.1213 | 6 | 18.03 | 1.03 | 0.4369 | 6 | 21 | 0.39 | 0.8794 |
| | | Date | 5 | 104 | 134.36 | <0.0001 | 5 | 104.2 | 29.37 | <0.0001 | 5 | 105 | 2.24 | 0.0556 |
| | | Treatment * date | 30 | 104 | 0,83 | 0.7171 | 30 | 104.2 | 0.95 | 0.5525 | 30 | 105 | 0.51 | 0.9817 |
| RF2 | 6.5.2019–13.5.2019 | Treatment | 6 | 18 | 1,61 | 0.2012 | 6 | 17.87 | 1.64 | 0.1929 | 6 | 18.12 | 1.45 | 0.2518 |
| | | Date | 6 | 125 | 177.17 | <0.0001 | 6 | 124.9 | 75.26 | <0.0001 | 6 | 125.4 | 1.20 | 0.3109 |
| | | Treatment * date | 36 | 125 | 0.67 | 0.9176 | 36 | 124.9 | 0.95 | 0.5540 | 36 | 125.3 | 1.43 | 0.0785 |
| RF3 | 10.9.2019–13.9.2019 | Treatment | 6 | 21.01 | 0.90 | 0.5102 | 6 | 18 | 0.70 | 0.6500 | 6 | 21 | 0.73 | 0.6319 |
| | | Date | 3 | 62.02 | 87.16 | <0.0001 | 3 | 63 | 20.37 | <0.0001 | 3 | 63 | 0.45 | 0.7183 |
| | | Treatment * date | 18 | 62.02 | 0.27 | 0.9985 | 18 | 63 | 0.92 | 0.5599 | 18 | 63 | 0.61 | 0.8788 |
| RF4 | 25.9.2019–27.9.2019 | Treatment | 6 | 18 | 1.22 | 0.3395 | 6 | 18 | 0.79 | 0.5912 | 6 | 18 | 1.05 | 0.4246 |
| | | Date | 3 | 63 | 61.62 | <0.0001 | 3 | 63 | 94.12 | <0.0001 | 3 | 63 | 0.56 | 0.6448 |
| | | Treatment * date | 18 | 63 | 1.72 | 0.0585 | 18 | 63 | 0.92 | 0.5555 | 18 | 63 | 1.44 | 0.1465 |

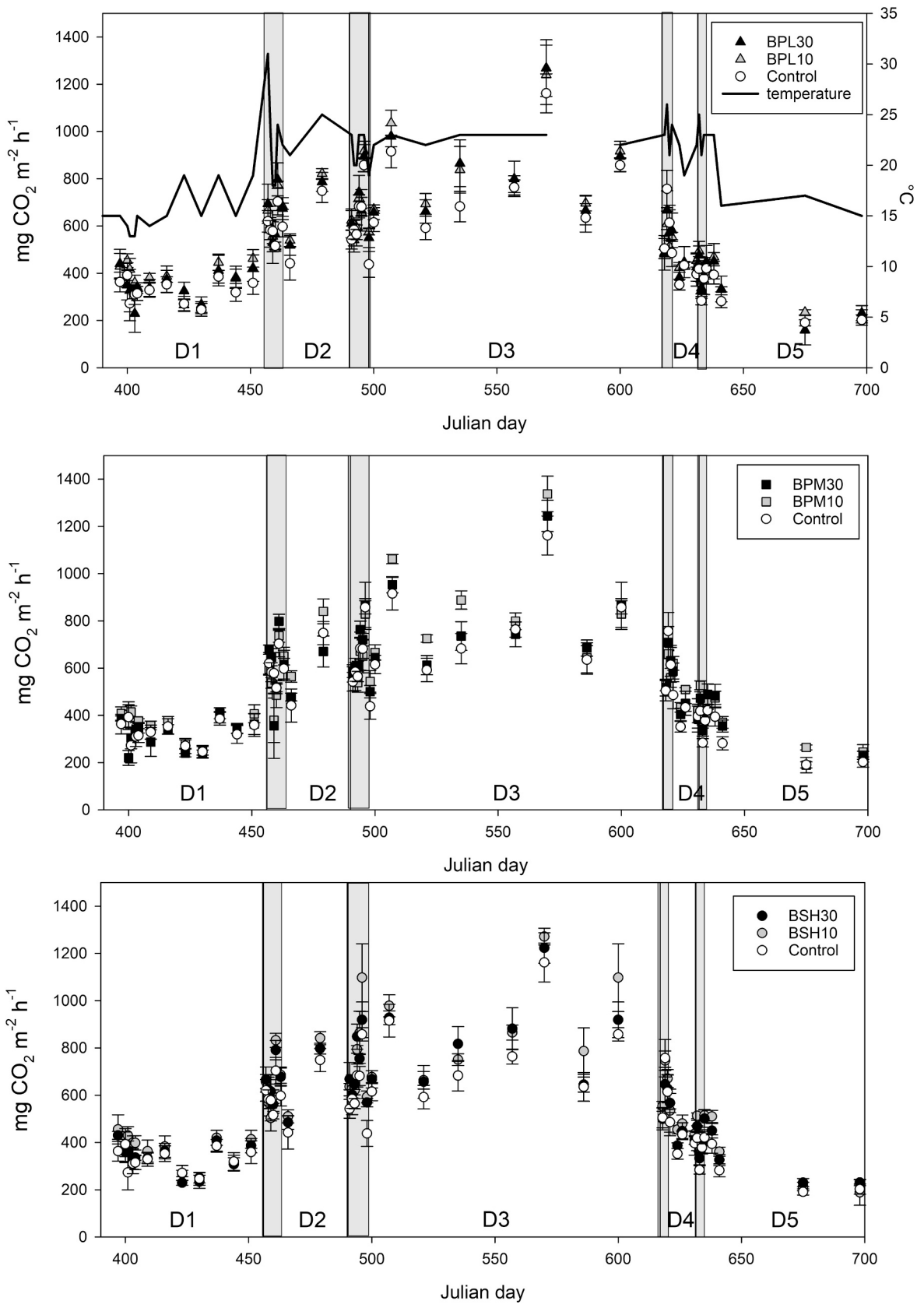


**Fig. 2.** Average (± standard error of mean) $CO_2$ emission in measuring days during the experiment. Acronyms D1–D5 indicate dry periods and gray areas rainfall events in order RF1, RF2, RF3 and RF4. The solid line in the uppermost panel indicates greenhouse temperature during the measurements (the scale on the right).

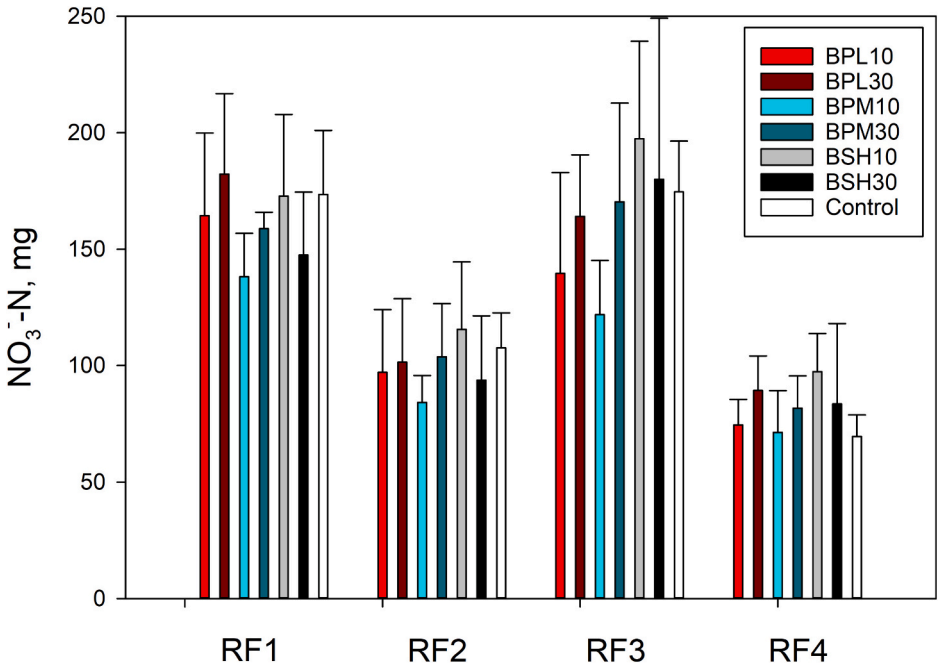


**Fig. 3.** Average (± standard error of mean) cumulative amount of $NO_3^-$-N in leached water during rainfall events (RF1–RF4).

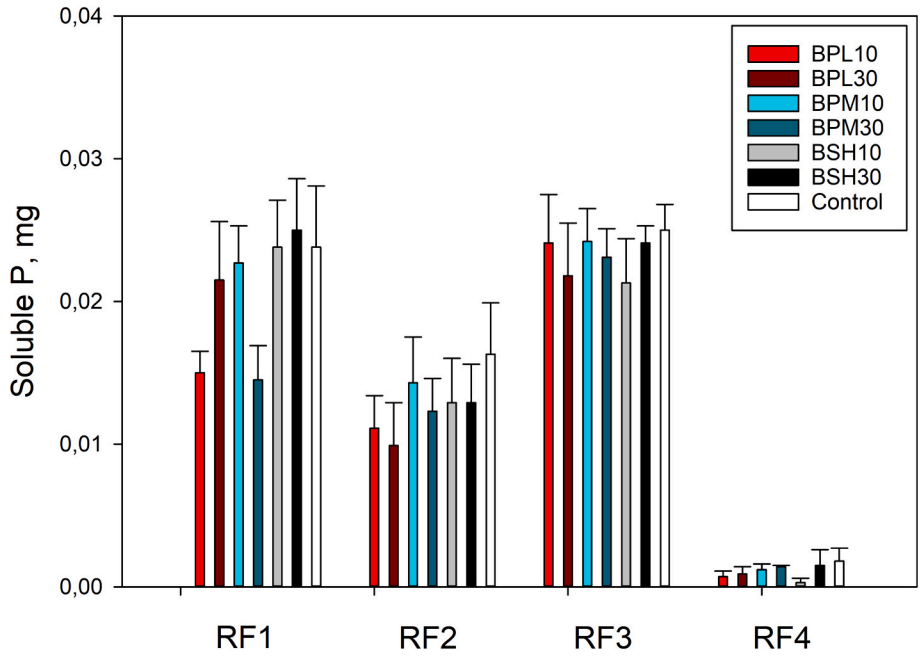


**Fig. 4.** Average (± standard error of mean) cumulative amount of soluble P in leached water during rainfall events (RF1–RF4).

fully unusual (Klemedtsson et al., 2009, Saarnio et al., *unpublished results*). High $N_2O$ emission peaks are mostly related to temporal changes in soil conditions favouring denitrification or gas diffusion, for example due to fertilization, freezing, precipitation or tillage (Maljanen et al., 2003a, Gerin et al., 2023), whereas annual emissions of peat soils are best predicted by the bulk density, C:N ratio and groundwater level (Klemedtsson et al., 2005; Liu et al., 2019). Our incubation of regularly watered, bare, highly degraded peat (von Post Humification Scale – H8 and bulk density 0.43 g $cm^{-3}$ at the depth of 0–20 cm), possessing with a low C:N ratio (18), and the soil cores were under warm conditions resulting in a combination of conditions that supported $N_2O$ production, and thus the high $N_2O$ emissions were anticipated.

In general, the biochar treatments did not mitigate $N_2O$ emissions (Table 3). On the contrary, the average $N_2O$ emission from BPL10 was the highest and differed significantly from the control on many days throughout the experiment. Considering the findings of some meta-analyses, it is not surprising that the biochars pyrolyzed from pine bark were not effective at reducing $N_2O$ efflux (Cayuela et al., 2014; Borchard et al., 2019), as they were both produced at low temperatures (350 and 450 °C). In addition, they were coated by pyrolysis oils, which could have reduced their ability to retain nutrients. This sorbed pyrolysis oil is a complex mixture of various organic compounds (Antal and Grønli, 2003) that could provide labile C for denitrifiers thus favouring $N_2O$ emissions in BPL10 for which we found increased emissions

**Table 4**
Generalized linear mixed model results for leached cumulative amount of nutrients (soluble P, $NH_4^+$-N, $NO_3^-$-N) and percolated water (ml), for water holding capacity of pure biochars, and for pH, cation exchange capacity, water holding capacity, electrical conductivity, calcium, phosphorus, potassium, magnesium and sulphur in soil at the end of the experiment.

| Effect | Num DF | Den DF | F value | Pr > F |
|---|---|---|---|---|
| Soluble phosphorus (P) | | | | |
| Treatment | 6 | 18 | 2.07 | 0.1076 |
| Rainfall period | 3 | 9 | 49.55 | <0.0001 |
| Treatment * rainfall period | 18 | 54 | 1.25 | 0.2576 |
| Ammonium ($NH_4^+$-N) | | | | |
| Treatment | 6 | 22.6 | 2.28 | 0.0715 |
| Rainfall period | 3 | 36.23 | 32.82 | <0.0001 |
| Treatment * rainfall period | 18 | 44.98 | 0.93 | 0.5491 |
| Nitrate ($NO_3^-$-N) | | | | |
| Treatment | 6 | 18.01 | 1.02 | 0.4424 |
| Rainfall period | 3 | 9.358 | 63.46 | <0.0001 |
| Treatment * rainfall period | 18 | 41.98 | 0.74 | 0.7528 |
| Percolated water (ml) | | | | |
| Treatment | 6 | 17.72 | 0.34 | 0.904 |
| Rainfall period | 3 | 7.01 | 757.23 | <0.0001 |
| Treatment * rainfall period | 18 | 37.33 | 0.98 | 0.5012 |
| WHC (pure biochars) | | | | |
| Biochar type | 2 | 2 | 11.94 | 0.0773 |
| pH | | | | |
| Treatment | 6 | 18.15 | 4.47 | 0.006 |
| CEC (biochar + soil) | | | | |
| Treatment | 6 | 17.88 | 3.03 | 0.0316 |
| WHC (biochar + soil) | | | | |
| Treatment | 6 | 18 | 2.21 | 0.0899 |
| Electrical conductivity | | | | |
| Treatment | 6 | 21 | 3.94 | 0.0086 |
| Calcium (Ca) | | | | |
| Treatment | 6 | 1 | 5.47 | 0.3162 |
| Phosphorus (P) | | | | |
| Treatment | 6 | 3.41 | 1.25 | 0.4491 |
| Potassium (K) | | | | |
| Treatment | 6 | 18 | 1.18 | 0.3604 |
| Magnesium (Mg) | | | | |
| Treatment | 6 | 18 | 1.15 | 0.3759 |
| Sulphur (S) | | | | |
| Treatment | 6 | 21 | 2.26 | 0.0772 |

compared to those of the control (Fig. 1). On the other hand, the characteristics of spruce biochar (high production temperature [600 °C], high C:N ratio [133] and high specific surface area [550 $m^2/g$]) should have reduced $N_2O$ emissions, but the characteristics of soil (low pH [5.2], high content of organic C [250–320 mg $g^{-1}$] and N [14–18 mg $g^{-1}$]) may have counteracted the mitigating biochar effect (Cayuela et al., 2014, Borchard et al., 2019). It has been concluded that the biochar addition would decrease $N_2O$ emission by increasing pH, by capturing nitrate and by affecting microbial community (Kammann et al., 2017). Therefore, in further studies, higher application rates of biochar with high pH should be implemented to test the functionality of liming and nitrate capture effect in peat soils.

### 4.2. Methane

Independent of the treatment, our bare peat profiles mostly consumed atmospheric $CH_4$ during the whole experiment, and the net emissions were negligible (<0.03 mg $CH_4$ $m^{-2}$ $h^{-1}$) (Fig. S1). The consumption rate (typically between −0.02 to −0.002 mg $CH_4$ $m^{-2}$ $h^{-1}$) was comparable to field measurements of boreal cultivated peat soils (Maljanen et al., 2003b; Regina et al., 2007). Some earlier studies have shown that biochar can enhance the uptake rate of $CH_4$ in cultivated mineral soils (Karhu et al., 2011; Kubaczyński et al., 2022), but meta-analyses indicate that biochar addition on average decreases $CH_4$ uptake in dry soils (e.g. Jeffery et al., 2016; Ji et al., 2018). The mechanisms by which biochars influence $CH_4$ consumption in soil have not yet been elucidated but biochar addition is expected to affect the microbial activities via porosity, pH, water retention, and alleviation of $NH_4^+$ inhibition (Jeffery et al., 2016; Wu et al., 2019; Zhao et al., 2021). In our peat profiles, no significant differences in $CH_4$ fluxes were found between the different biochars or biochar application rates (Table 3). It is possible that opposite mechanisms overturned each other or more likely that the peat has initially so different properties (high porosity and water retention, high N availability, high buffer capacity) compared to mineral soils that application rates effective in mineral soils are not high enough to induce any changes in the soil properties potentially affecting $CH_4$ consumption in peat soil.

### 4.3. Carbon dioxide

The addition of biochar to soil has often been observed to first increase the total $CO_2$ efflux, because the labile C compounds of biochar and/or of soil decompose following biochar addition (Maestrini et al., 2015; Saarnio, 2016; Wang et al., 2016). A similar increase was not consistently seen in our peat soil, although some treatments on individual measuring dates were different from the control (Fig. 2). For example, when 10 % biochar (by volume) was added to peat soil, soil respiration increased significantly for an entire incubation period of 60 days (Messiga et al., 2022). Probably the amount of new labile carbon compounds in our biochar addition (<1 wt%, 1–4 % volume %) was small compared to the decomposable material in cultivated peat soil that its decomposition was not distinguishable from the high rate of peat decomposition. Our soil respiration rate varied mainly between 250 and 650 mg $CO_2$ $m^{-2}$ $h^{-1}$ (Fig. 2) resembling rates observed in the boreal peat fields during the snow-free season (Lohila et al., 2003; Alm et al., 2007). However, the regular moistening and high air temperature in the greenhouse (occasionally between 25 and 30 °C) enhanced the decomposition rate up to 1300 mg $CO_2$ $m^{-2}$ $h^{-1}$. The warm conditions for the whole peat profile, possibly enhanced the decomposition of deeper layers (Liu et al., 2016) and thus these results are not comparable to those in field conditions. The high decomposition rate may have masked the possible biochar-induced changes in the $CO_2$ release at the top of the profile.

### 4.4. Nutrient leaching

The $NH_4$-N concentrations (range 0–5.8, mean 0.4 mg $L^{-1}$) in water percolated through the peat columns were comparable, but the $NO_3$-N concentrations (range 0–732, mean 125 mg $L^{-1}$) were mainly much higher than the concentrations observed in waters collected from subsurface drains of a boreal peat field (Pham et al., 2023). As the soil was not fertilized during the experiment and the highest concentrations were observed during the last rainfall event (RF4), the high amount of leached $NO_3$-N reflects the high N release from peat during the decomposition of monoliths under warmer conditions as the whole 0–60 cm peat column was exposed to ambient temperature.

Both $NO_3^-$ and $NH_4^+$ can be retained on the ion exchange sites of biochars, and thus biochar amendment has the potential to alleviate leached nutrient losses (Fidel et al., 2018). However, our biochars did not reduce nutrient leaching. As the pine bark biochars were covered by pyrolysis oil, it is not surprising that they did not decrease N leaching. Instead, similar kind of spruce biochar as that used here (a high specific surface area and C:N ratio) decreased $NO_3^-$ leaching both as pure biochar and as mixed in mineral soils (Saarnio and Kettunen, 2020), but in this peat soil no significant effect was observed. In the earlier experiment, however, the retention effect decreased when the $NO_3^-$ concentration in solution around the biochar increased, and in this experiment the $NO_3^-$ concentrations in the percolation water were clearly higher than those in the study of Saarnio and Kettunen (2020). Thus, the high availability of $NO_3^-$ might have faded the possible retention effect (see also Borchard et al., 2019; Lévesque et al., 2020). In addition, the pH of our biochar (8.0) was lower than that of the spruce biochar in the earlier experiment (10.9), which according to the meta-analysis of Borchard et al. (2019) indicates increasing $NO_3^-$ leaching. Most of the earlier studies have, however, been conducted on mineral soils and further studies in peat soils are needed. High application rate (>40 Mg $ha^{-1}$) of non-wood biochar pyrolyzed at high temperature (>500 °C) and possessing low pH (<7.8) could be recommended for the next nitrate leaching study with peat soils (Fidel et al., 2018; Borchard et al., 2019), whereas higher application rate of biochar with high pH and low production temperature would benefit ammonium adsorption (Fidel et al., 2018; Zhao et al., 2022).

The soluble P concentrations (range 0–0.1, mean 0.02 mg $L^{-1}$) in the water percolated through the peat columns were comparable to the concentrations observed in waters collected from subsurface drains of a boreal peat field (Pham et al., 2023). The highest concentrations were in the first collected percolation water and then the concentrations remained low during the rest of the experiment. According to the review of Almanassra et al. (2021), the phosphate sorption capacity of conventional biochars not rich in metals, as our biochars, is low. Thus it is not surprising that P leakage from peat profiles was not decreased by any of the biochar treatments. Some biochars can first even increase P leaching due to the P release from fresh biochar (Saarnio and Kettunen, 2020) or due to the biochar induced increase in soil pH (Saarnio et al., 2018). In this study the changes in soil P and pH were negligible after biochar additions and P leaching remain unaffected in all biochar treatments.

### 4.5. Soil properties

The water holding capacity of our peat soil was not affected by any of the biochar treatments. The observed relationships between soil organic matter content with porosity and water retention (see Walczak et al., 2002) indicate that the organic matter content of our peat soil was so high that its porosity is sufficient to almost maximal possible water retention and thus it is not surprising that a small amount of biochar (<1 % of soil weight) did not improve the water holding capacity and nutrient retention. Correspondingly, the cation exchange capacity in the topsoil did not markedly change in the biochar treatments compared to that of pure peat (Table 1). The CEC for our peat soil was rather low but within the range of CECs measured for 37 peat samples from Finnish cultivated and undrained peatlands (Räty et al., 2021). As the CEC of the biochars sharply decreases when the pyrolysis temperature increases (Gomez-Eyles et al., 2013; Domingues et al., 2020), the CEC of our only non-oil-covered biochar (BSH) was probably even lower than that of the peat. In any case, the small biochar additions did not affect $NH_4^+$ leaching from the peat monoliths (Fig. S2).

## 5. Summary/conclusion

Pine bark and spruce biochars had only weak and inconsistent impacts on gas fluxes and no significant short-term effect on nutrient leaching from peat soil with these application rates. These results indicate that the observations from studies conducted in mineral soils cannot be directly extrapolated to peat soils. Peat actually has many of the characteristics (related to e.g. water holding capacity, cation exchange capacity, elemental content or surfaces for microbes) that are pursued by adding biochar and it is thus understandable that the effects of biochar addition remain minor if these characteristics affecting gas fluxes and nutrient leaching do not significantly change. Based on these results, moderate softwood biochar additions (10 or 30 Mg $ha^{-1}$) do not help to reduce GHG emissions and nutrient leaching in agricultural peat soils in the short term. The higher application rate of high temperature biochar is recommended for further studies with peat soils. In field conditions, however, the use of biochar is very expensive and other managements like raising of water level could be more useful option for mitigating environmental impacts of peat soils.

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## CRediT authorship contribution statement

**S. Saarnio:** Writing – original draft, Visualization, Formal analysis. **H. Kekkonen:** Writing – review & editing, Methodology, Investigation, Formal analysis, Conceptualization. **K. Lång:** Writing – review & editing, Validation, Project administration, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization.

## 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.

## Data availability

Data will be made available on request.

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