The use of biochar to enhance carbon sequestration in peatlands.

FEARNS-NICOL, EMILY,ELIZABETH

THE USE OF BIOCHAR TO ENHANCE CARBON SEQUESTRATION IN PEATLANDS.

Emily Elizabeth Fearns-Nicol

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Department of Earth Sciences

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Abstract

Peatlands are vast stores of carbon (C) but sequester C slowly relative to the rate of anthropogenic climate change. To maximise the considerable C storage potential of peatlands, this study assessed whether applying additional C to a peatland would enhance it as a C sink. Biochar is a refractory form of C which is formed from pyrolysis of woody biomass and is often proposed as a nature based C store. Biochar has never been applied to a peatland before so its effects on peatland water quality, gas fluxes and vegetation were not known.

This study assessed the impact of biochar application on a lowland raised bog through measurement of water quality, gas flux, and vegetation indices. Analysis of water quality found that, although biochar caused significant changes in some parameters, these changes were small and within the range of other peatland settings: therefore, not making any tangible difference to the function of a peatland. Similarly, increased positive net ecosystem exchange (NEE) flux into the atmosphere was a small increase relative to the amount of C stored by adding biochar to the peatland. Vegetation growth was not detrimentally changed: within 15 months native vegetation had grown to pre-treatment levels.

As there was no detrimental change to any of water quality, gas flux or vegetation after the application of biochar it was possible to calculate the residence time of biochar after being applied to the peatland. The application of biochar would store an additional 328.5 g $CO_2/m^2/yr$. Assuming CO_2 fluxes continued at the same rate as after biochar was applied, it would take 240 years for the additional C applied within the biochar to be released from the peatland. Additionally, as peatlands form slowly, the addition of biochar to the surface would be equivalent to 10 to 20 years of peat growth.

The UK government are aiming to achieve NetZero by 2050. As peatlands are the largest store of organic carbon in the terrestrial biosphere, they have an important role to play in achieving this goal. Biochar proved to be successful in enhancing C storage in peatlands, the implications of applying biochar to peatlands are more likely to be economical than biogeochemical.

Declaration and copyright

I confirm that no part of the material presented in this thesis has previously been submitted by me or any other person for a degree in this or any other university. Where relevant, material from the work of others has been acknowledged.

Signed:

Emily Elizabeth Fearns-Nicol

Date:

21st November 2024

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1. Introduction

1.1 Peatlands characteristics

Peatlands are nutrient deficient environments, formed through the in-situ accumulation of semi-decomposed organic material, whereby the rate of primary productivity exceeds the rate of decay of organic matter (Lacourse et al., 2019). This ongoing process in a peatland environment is promoted through acidic conditions and stable water table levels limiting microbial activity by reducing oxygen levels, therefore limiting the decomposition of organic material, resulting in peat accumulation (Moore and Knowles, 1989).

Peatlands are classified by their hydrology being either fed by precipitation or groundwater (Holden, 2006). Lowland raised bogs are generally ombrotrophic meaning their water source is primarily precipitation. The formation of peat happens in areas where the rainfall or ground water influxes are greater than evaporation because peatlands are formed through the partial decay of organic matter in water saturated environments (Holden, 2006). Hydrology directly impacts various aspects of a peatlands in particular the C storage of peatlands. One of the reasons that peatlands accumulate C is due to high and stable water tables that prevent the influx of fresh water into the soil pore spaces, demonstrating the control hydrology has on redox processes of a peatland (Holden, 2006).

It is estimated that 150 Gigatonnes of Carbon (Gt C) are stored in global peatlands (Yu, 2012) and 1.74 Gt C in UK peatlands (Joosten, 2009). Despite peatlands storing large amounts of atmospheric CO_2, they absorb CO_2 relatively slowly (Page and Baird, 2016). The carbon balance within peatlands is determined by measuring the fluxes of all forms of C (C lost or gained). Including: dissolved organic carbon (DOC), dissolved inorganic C (DIC), gaseous C (CO_2 and CH_4) and particulate organic C (POC) (Worrall et al., 2003). Continued accumulation of organic matter means atmospheric CO_2 continues to be sequestered, meaning peatlands act as a long-term carbon sink (e.g. Alexandrov et al., 2020). However, at present carbon is being accumulated at an average of 0.02 to 0.03 kg CO_2-C m^{-2} y^{-1} in the last 5000-10,000 years (Frolking et al., 2001). Peatlands store 30% of the earth's total organic C, however in some cases peatlands are degraded meaning they are emitting greenhouse gases rather than storing them. When peatlands are degraded through burning or extraction for example, they release C and or methane. Peatland accumulation rates are small relative to the timescales required to reverse anthropogenic climate change and to achieve NetZero by 2050, hence there is a need to enhance C sequestration. Peatlands are the largest terrestrial store of carbon on earth as such they have an important role of play in achieving the UK government's targets of NetZero by 2050. Peatlands are a nature based solution to NetZero, though there are many nature based solutions there are also alternatives which deal with systemic reductions of carbon emissions across sectors in the UK.

1.2. Biochar

Biochar is a carbon rich, fine grained material derived from the thermal decomposition (pyrolysis) of organic matter at > 700 ^{o}C in the absence of oxygen (Weber et al., 2018), a similar way to the production of charcoal (Lehmann and Joseph, 2015). The chemical content of biochar is more variable than the methods used to produce it. Chemical and C content of biochar varies depending on different factors, such as pyrolysis temperature and the origin of the organic matter used to produce the char: typically, C content is > 70% (Lehmann and Joseph, 2015).

1.3. Existing application of biochar

To date there is no literature that has applied biochar onto peatlands, though this is the case, biochar has been used on constructed wetlands to enhance the potential for contaminant removal (Chen et al., 2021). Studies that apply biochar to a constructed wetland are useful in indicating the behaviour of biochar on a wetland, a somewhat similar environment to peatlands. Studies applying biochar to constructed wetlands often assess water quality but mostly limited to pH and nutrient concentrations. Gupta et al. (2015) monitored the application of biochar on a constructed wetland and monitored pH, nitrate, phosphorus and biomass growth after biochar application. They observed a significant increase in pH after application due to the alkaline nature of biochar. Cayuela (2013) showed that biochar facilitated denitrification, and Gupta et al. (2015) found a significant reduction in nitrate concentration after biochar application to a constructed wetland. Similarly, Huett et al. (2005) found that biochar has the capacity to adsorb phosphorus, and Gupta et al. (2015) noted a significant reduction of phosphorus in some plots after biochar application, however, the importance of vegetation as a temporary store of phosphorus could be contributing to the reduction in phosphorus concentration.

As well as biochar being applied to constructed wetlands, it has also been applied to other soil types such for example, mineral soils and organic soils. It is often applied on agricultural soils as a means of enhancing the fertility of the soil. Many studies applying biochar to mineral soils look at the effects on the soil itself and the water leaving the soil, whereas few studies report on the effect of biochar on soil pore water. Biochar, as an alkali material, is often used to deliberately increase the pH of soils (e.g., Geng et al., 2022).

Though the stability of biochar on peatlands has not been studied, the stability of biochar application on other soil types has been assessed (Wang et al., 2022). Biochemically, biochar is very stable and theoretically can stay within soil for a long time, due to its chemically stable components (Lehmann et al., 2012). Long term stability of biochar is vital for its contribution to carbon sequestration and storage, as it determines for how long the C applied to the soil in the form of biochar will remain sequestered (Lehmann et al., 2012; Wang et al., 2022). Overall, the stability of biochar on soil is largely dependent on the pyrolysis temperature and burn time used to make the biochar (Lehmann et al., 2012).

Biochar applied to mineral and organic soils are often monitored in terms of actual soil quality, and quality of the water leaving the soil. No studies, to date, however, have investigated effect of biochar on soil pore water chemistry. Biochar has been applied with the aim of increasing the pH of acidic agricultural soils, which was found to be successful by several studies (e.g. Chintala et al., 2014; Singh et al., 2022; Geng et al., 2022). The results of studies looking at the effect of biochar application on mineral soils are more equivocal. Nawaz et al. (2021), and Kane et al. (2021) reported a decrease in conductivity of water leaving the soil. While Chintala et al. (2014) and Joseph et al. (2015) observed a significant increase in conductivity of water leaving the soil after biochar application. Similarly, some studies reported a significant increase in dissolved organic carbon (DOC) of water leaving the soil after biochar application (Zimmermann et al., 2011), whereas others showed a significant decrease in DOC concentration of water leaving the soil. Mineral soils are often rich in nutrients. Studies applying biochar to soil generally saw a decrease in nutrient concentration of water leaving the soil due to nutrients being absorbed and retained by the biochar (Sohi et al., 2010).

Some studies that apply biochar to the surface of mineral and organic soils reported increased CO_2 fluxes of 7.4% (Jia et al., 2023) or 20% (He et al., 2017) to the atmosphere. Whereas Mukherjee and Lal (2013) reported no significant change in CO_2 fluxes after biochar application, and Abagandura et al. (2019) reported a decrease in flux into the atmosphere. It should be noted that even with increased fluxes into the atmosphere the reported C pool within the soil increased due to biochar application, e.g. by 38.1% in an upland soil (Jia et al., 2023). Azeem et al. (2019) found that biochar stimulated the release of CO_2 into the atmosphere. Net ecosystem exchange (NEE) increased by 200% and 147% at two points during the first year of biochar addition to one crop type (Azeem et al., 2019). However, when biochar was added to a different crop, no significant difference in NEE flux was observed during the first year of biochar addition, but there was a decrease in NEE of 46.8% to 37.9% during the second year after application (Azeem et al., 2019).

It should be noted that the biochar applied to both mineral soils and constructed wetlands is often made from different biomass sources and produced at varying pyrolysis temperatures. Such differences may mean the biochar varies between production. Variations in biochar may explain some of the differences between experiments and results, in terms of water quality and gas fluxes from constructed wetlands and mineral soils.

1.4. Evidence of charcoal in peatlands

Biochar has not been applied to a peatland for C sequestration purposes before, however, there is evidence of charcoal within peat cores from around the world. Previously found during paleoclimatic studies, the presence of charcoal has been found in the UK (Innes et al., 2004); the USA (Tanner et al., 2018); Sweden (Cui et al., 2020); Spain (Schellekens et al., 2015); Norway (Kasin et al., 2013) and Serbia (Fuerdean, 2021). Though direct studies of biochar persistence in peatlands do not exist, charcoal in some of these cores is suggested to have survived 1000s of years (Lehmann et al., 2022). Though persistence of biochar is not known, Innes et al. (2004) suggest the nature of charred material within peat cores indicates the scale and duration of past fires. Determining the duration and scale of past fires would be useful for understanding the residence time of biochar within peatlands.

1.5. Peatland management

Though not performed before, applying biochar to a peatland is a form of management. There are a range of management techniques that have been applied to peatlands, where the effects on peatland water quality has been assessed. Peatlands are mainly controlled by their hydrology, dominated by a relatively high and stable water table, and require these conditions to function optimally (Gatis et al., 2023). Peatland management often alters the nature of the water table and so impacts upon water quality would be expected. The reported effects of peatland management depend on the study site and technique applied, there is no consistent result whereby one type of peatland management causes a detrimental change to all areas of peatland water quality. Instead, a range of results have been reported, sometimes even within the same experiment across different parameters.

Peatlands are areas of low pH due to acids being released from the process of organic matter decomposition (Shotyk, 1998). Native peatland vegetation such as sphagnum moss contribute to the acidic nature of a bog due to the cation exchange through sphagnum growth which is important for the partial decomposition organic matter and the formation of new peat (Antala et al., 2022). Several studies have assessed the impact of various types of peatland management on pH. Revegetation is a type of peatland management whereby native vegetation, such as sphagnum moss is planted into a peatland, reintroducing the vegetation to the peatland (Peacock et al., 2013). In successful revegetation the plant species will establish itself and continue to grow and spread across the landscape, in the hope of dominating the landscape with native vegetation, as opposed to invasive species such as birch trees. Qassim et al. (2014) found that revegetation caused a significant decrease in soil water pH on revegetated peatlands compared with bare peat, whereas grazing was found to have no significant impact on soil water pH (Worrall et al., 2007). Rewetting had more equivocal impacts - Fenner et al. (2011) found a significant increase in pH following rewetting, whereas Wilson et al. (2014) observed a decrease in soil water pH after rewetting by ditch blocking.

As well as being areas of low pH, bogs are predominantly fed by rainwater which has a low electrical conductivity, and as such, peat soil waters often have low conductivity: The conductivity value of peatland pore water is close to the conductivity of rainfall (Worrall et al., 2003). Qassim et al. (2014) and Wilson et al., (2014) observed a significant decrease in conductivity after revegetating and rewetting, respectively, whereas Worrall et al. (2007) observed no change in conductivity following grazing.

The impact of peatland management on peatland DOC is widely reported because DOC is not only a component of the carbon cycle of these high carbon ecosystems but is also a major water quality limitation from peat-covered catchments (Worrall et al., 2009). The DOC concentration of peat soil water is important for water quality of flow from the bog. Detrimental changes in soil water DOC, particularly increased concentration of DOC has been associated with increased atmospheric temperatures (Bottrell et al., 2004). Ombrotrophic peatlands have their nutrients fed predominantly through rainfall and atmospheric input. Ground water has very little influence on the hydrology (Oikos, 1978). Within ombrotrophic bogs, increased DOC concentration has been linked with the rise, and subsequent decline, in atmospheric pollutants (Bottrell et al., 2004). Ward et al. (2007) found that grazing significantly increased the DOC concentration of soil water. Similarly, Trinder et al. (2008) found revegetation to significantly increase DOC concentration, whereas Evans et al. (2006) found revegetation to cause no significant change in DOC concentration. Many studies report no significant difference in soil water DOC concentration after ditch blocking (Wilson et al., 2014; Evans et al., 2018; Peacock et al., 2018).

Peatland management techniques have the potential to bring nutrients onto what are typically nutrient deficient environments. Ombrotrophic peatlands are particularly deficient in nutrients as their only source of nutrients is from rainfall and the low nutrient availability from slow organic matter decomposition (Wang et al., 2015). The naturally low nutrient availability is important for the flora growing on bogs as these thrive in such conditions. An increase in nutrient availability may bring about new invasive flora, and or cause a poor growth of native vegetation (Heijmans et al., 2008).

The fate of peatlands relies on the balance of plant primary productivity and oxidation of organic matter. Oxidation requires a terminal electron acceptor (TEA). The most energetically favourable TEA is O_2 followed, in order of reducing energy return, by NO_3, Mn, Fe, SO_4, and CH_4. Ultimately, the organic matter itself can be become a TEA: fermentation and methanogenesis will occur with the concomitant production and release of methane (CH_4), which is an even more powerful greenhouse gas then CO_2

(Lair, 2009). Therefore, the fate of the organic matter turnover in peatlands is related to the supply of TEAs. There is, however, a lack of studies assessing TEAs within soil pore water. Fenner et al. (2011) found a significant increase in iron concentration of peat soil water following rewetting, but other approaches of peatland management have not accounted for TEAs. Boothroyd et al. (2021) assessed the TEA budget of a peatland and found that the concentration of sulphate varied with depth, meaning sulphate in some reductive form was still present within the peat. Whereas nitrate was not present at any depth meaning that nitrate had been used up near to the surface of the peatland (Boothroyd et al., 2021). The supply of TEAs within a peatland relies on the hydrologic conditions: a high water table alone is not sufficient, there needs to be stagnant water table so that fresh supplies of TEAs including oxygen are not brought into the pore space and equally, that reaction products are not removed.

Previous peatland management studies typically aim to restore degraded peat which may subsequently enhance C sequestration, rather than aiming to enhance C sequestration directly (Worrall et al., 2009). Therefore, it is important that C fluxes are monitored to understand whether implemented peatland management do not detrimentally affect C accumulation rates within the peat. With respect to carbon gas fluxes, revegetation was found to significantly increase GPP due to increased C uptake by (e.g. Worrall et al., 2011). However, the reported effects of revegetation on NEE and NER were varied. Trinder et al. (2008) found a significant increase in both NER and NEE, Keller et al. (2005) found a decrease in NER and Evans et al. (2006) found no significant change in NEE fluxes. Grazing was reported to significantly increase GPP and NER (Ward et al., 2007). Rewetting of peatlands, for example by blocking of drains, suppresses mineralisation to CO_2 (Wilson et al., 2016; Kreyling et al., 2021). Schimelpfenig et al. (2014) observed a significant increase in NEE fluxes after ditch blocking due to an overall increase in GPP. Both Schimelpfenig et al. (2014) and Green et al. (2018) observed no change in ecosystem respiration, however, Gatis et al. (2020) found a significant decrease in ecosystem respiration, but no significant change in photosynthesis after ditch blocking.

Native peatland vegetation growth is important for the formation of peat and function of existing peatlands (Belyea and Malmer, 2004). Revegetation is a common management technique for increasing the cover of native vegetation, that are known as peat forming species, such as sphagnum moss (e.g. Rydin et al., 2006). Albedo has been used as a measure of the change in incoming energy across an area, typically comparing bare peat with vegetated peatlands (Worrall et al., 2022). Albedo has previously been used as an indicator to understand how non-vegetated peat had a warming effect (Worrall et al., 2022).

1.6. Managed peatland burning

While multiple studies have assessed the impact of management and restoration on water quality and the carbon balance of peatlands, there are none that report biochar addition to enhance C storage. The nearest studied analogy to biochar addition to peatlands is managed burning and wildfires on peatlands, because these will result in biochar being left on the surface of the peat (Clay and Worrall. 2011). The burning of peatland vegetation results in the addition of biochar to the peat surface, although this is being achieved by simultaneous removal of shrubby vegetation.

A range of impacts from managed burning have been studied. The depth to the water table was found to have significantly decreased after managed burning, i.e. water table became closer to the surface (Worrall., 2007; Clay et al., 2009; Brown et al., 2014). Other impacts are less clear. Worrall et al. (2007) reported a significant increase in soil water pH after prescribed burn management, whereas Brown et al. (2014) found no significant change in peat soil water pH. Qassim et al. (2014) and Worrall et al. (2007) reported a significant increase in soil water conductivity, whereas Fisher et al. (2006) found no significant difference in conductivity after burning. Clay et al. (2012) and Worrall et al. (2013) found no significant difference after burn management. Whereas Helliwell et al. (2010) found DOC to significantly decrease after managed burning. Managed burning was found to have decreased the iron concentration of soil pore water (Clay et al., 2010; Worrall and Adamson, 2008; and Clay et al., 2009). Some studies found an increase in nitrate concentration of soil pore water after burning (Clay et al., 2010; Clay et al., 2009) whereas Worrall and Adamson. (2008) found a decrease in nitrate concentration after managed burning. Though there are studies on the impact of managed burning, there are no studies assessing the impact of wildfire on peat porewater quality because it is very difficult to establish appropriate controls, i.e., it is unclear when and where a wildfire will occur.

Peatland GPP was found to have significantly increased after managed burning (Ward et al., 2007; Clay et al., 2010). Clay et al. (2015) reported a significant increase in NEE after burning, but no significant change in NER after burning, whereas Ward et al. (2007) report a significant increase in NER and GPP compared to unburnt plots. As would be expected, albedo significantly decreased after managed burning (e.g., Thompson et al., 2015). Burning was found to significantly change the species of vegetation present on the peatland, observing an increase in graminoid vegetation and a reduction in shrub vegetation (Ward et al., 2007).

Burn management results in charred biomass being left on the surface of the peatland (Clay and Worrall, 2011). However, there are discussions as to whether the charred biomass left after burning increases C accumulation. Heinemeyer et al. (2018) suggest charcoal from burning contributed to an observed increase in net C accumulation. Whereas Brown et al. (2015) suggested that managed burning does not increase net C accumulation, but instead negatively impacts peatland chemistry and hydrology. Davies et al. (2016) found charred peatland material from managed burning reduced the loss of C from a peatland but did not improve the sequestration rate of C from the atmosphere.

Ultimately, peatlands are large stores, but slow sinks of C relative to the rate of anthropogenic change. Current peatland management techniques are, to some extent, effective in managing and restoring damaged peat, but do not attempt to significantly increase the rate at which C is sequestered by peatlands. If 2050 NetZero goals (UK Government, 2023) are to be achieved, peatlands have an important role to play as the biggest terrestrial store of C. However, at present peatlands do not sequester enough C quickly enough. Applying biochar to the surface of a peatland could increase both the amount and the rate of C sequestration. However, the impacts biochar application can have on a peatland are unknown. This study, therefore, aimed to assess the fate of biochar on a lowland raised bog as well as assessing the effect of biochar application on water quality, the exchange of CO_2, and the growth of vegetation.

1.7. Aims and objectives

1. A number of concerns have been raised with respect to the impact of biochar application on water quality in wetland systems. This study aims to assess these concerns for a lowland raised bog. Specifically,
    a. Biochar is an alkali material; peat soils are typically acidic and so the addition of alkali biochar could disrupt the stability of the peat by increasing its pH.
    b. Biochar is an absorptive material and so could bring contaminants on to the site or could limit the movement of anions, cations and dissolved organic carbon (DOC) within the peat environment.
    c. Peatlands are typically nutrient poor environments and biochar has been associated with modifying and enhancing nutrient availability within soils.
2. This study aims to assess the effect of biochar application on the exchange of CO_2 from the peat. Biochar is being applied to peat to enhance carbon storage and so this study will test whether that is the case. Specifically,
    a. Whether biochar detrimentally changes the exchange of CO_2 of a lowland raised bog. The exchange of CO_2 for peat soils this includes the net ecosystem respiration (NER); net ecosystem exchange (NEE); and gross primary productivity (GPP).
    b. Using albedo and fixed position photographs were to monitor vegetation growth and the fate of biochar on the surface of the peatland.

2. Fieldsite characteristics

2.1. Field site

Hatfield Moors[1] is a 13.6 km^2 lowland raised bog, characterised by a series of former dug over peat cells. The chemical composition of the peat at Hatfield is given in table 2.1. Hatfield Moors together with Thorne Moors, north of the site, form England's largest lowland raised bog (Figure 2.1) (Natural England, 2019). Hatfield is surrounded by arable land on former flood plains of rivers feeding the Humber estuary with all sites in this study within 10 metres of sea level (Natural England, 2019). Primary peat formation at Hatfield occurred after a time of sea level rise approximately 4,500 years ago (Eversham, 1991), resulting in rivers in the area to back up, causing peat to accumulate on exposed mineral soils (Lacourse et al., 2019; Natural England, 2019). Native vegetation on the site is dominated by *Sphagnum* spp (moss) and *Eriophorum* spp (cotton grass). The onset of peat accumulation at the site is estimated at 3580 ± 108 calendar years BP (Shotton and Williams 1973).

Exploitation of peat from the site began with drainage of the region in the 1630s, and peat extraction for mostly horticultural purposes from 1945, prior to which depths of peat on the site were up to 6.1 metres (Worrall et al., 2022). Hatfield Moors was purchased by Natural England (then called English Nature - UK government's nature conservation agency) in 2004. When restoration began average peat depth across the site was 50 cm (Natural England, 2019). Restoration began in 2004 with drain blocking to raise water table depths. In 2013, a second phase of restoration began with the removal of scrub, classified as being an invasive species, which had taken over and had crowded out important native vegetation. Current estimated average peat depth across the site during restoration is 75 cm (Pers. Comms Natural England, 2022).

Hatfield Moors is a suitable site for this study as it is a large area of extracted peat, where an estimated 5 metre peat depth loss across the site meaning there is a capacity to raise the surface of the bog to allow for a restored surface. Additionally, Hatfield together with Thorne (a few km north of Hatfield) are the largest area of lowland raised bog in the UK, and therefore an important area of carbon storage for the UK. At present they are degraded and absorb carbon relatively slowly, so there is a need to restore a functioning bog surface.

Figure 2.1. The location of Hatfield Moors.

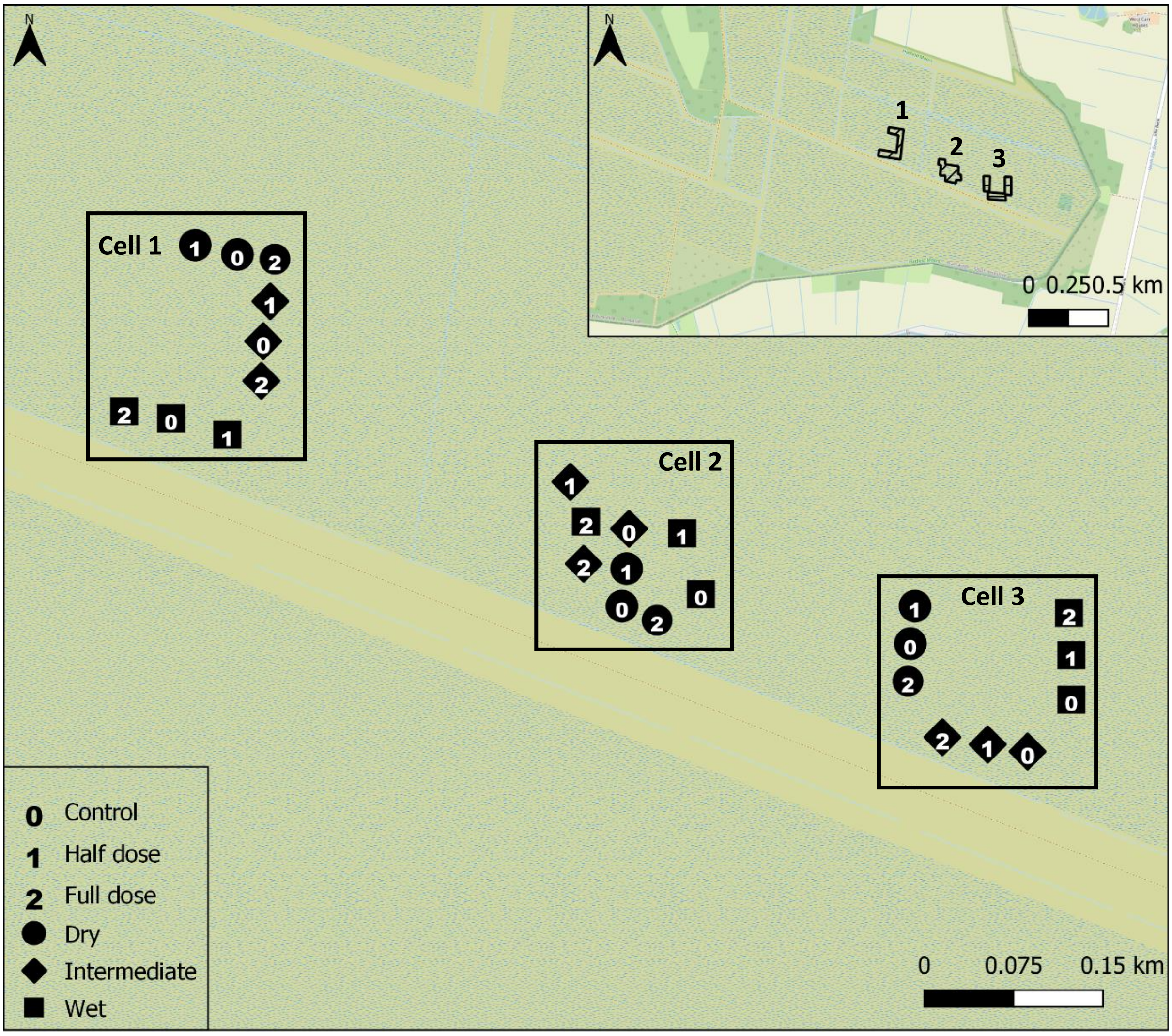

Figure 2.2. The location of plots used in this study. Representing the Location factor (Dry, Intermediate and Wet) and dose of biochar applied.

2.2. Experiment design

Hatfield biochar experiment consisted of treatment and control plots across the cells of the Moors (Figure 2.1; 2.2). The experiment followed a triplicated random block design, consisting of four factors.

The first factor was cell (Figure 2.3; 2.4) (henceforward referred to as Cell) which was the difference between three cells where the plots were located. There was no evidence of hydrological connection between the three cells.

The second factor was the location within the water table frame (henceforward known as Location) and it had three levels referred to as: dry (Figure 2.5) – the deepest water tables relative to the peat surface and so are the driest plots; wet (Figure 2.6) – have the shallowest water tables relative to the peat surface and so be the wettest plots; and intermediate (Figure 2.7) – having a water table between the dry and high water tables. Position of plots within the water table frame was judged at the start of the experiment and confirmed during the experiment.

The third factor was rate of biochar application (henceforward referred to as Treatment factor) and this had three levels. The three levels of biochar application were: full dose (64000 kg char/ha); half-dose (32000 kg char/ha); and control (no added biochar).

The fourth factor was the seasonal variation across the year after treatment (henceforward referred to as Month) with 15 levels, one for each monthly sampling visit post treatment. In total there were 27 plots.

The plots were established on 6/02/2022 With biochar applied on 15/02/2022. Thereafter, the plots were visited at least monthly from February 2022 until May 2023, with the first sampling visit on 07/02/2022 and the last sampling visit on 02/05/2023.

Each plot was formed of a 2 m by 2 m wooden perimeter, with the wooden perimeter used to ensure that the biochar was retained within each plot after application. Each plot contained one gas collar, and at least one dipwell. On each visit, the following measurements were taken: CO_2 gas flux; water table depth; a soil water sample was extracted from the dipwell; albedo; and a fixed position photograph. The albedo and fixed position photography were taken over the same corner of the plot and when accessing the plots a specific pathway was used to minimise disturbance and preserve the area. Figure 2.6. shows the setup of one example plot, showing the wooden perimeter, the gas chamber on the gas collar and the dipwell within the plot.

Biochar used in this trial was supplied by Caradoc Charcoal Ltd, Shropshire, UK, sourced from ash trees (*Fraxinus excelsior*) from sustainably managed forest. The biochar was produced at 550 ℃ in a batch pyrolysis process. The characteristics of this biochar are given in in the appendix, Table1. The feedstock of biochar used in this study was ash, however, the original source does not significantly change the properties of the biochar (Downie et al.,2009). The pyrolysis temperature and burn time affect the properties of biochar (Downie et al., 2009; Kazemi Shariat Panahi et al., 2020). Burn time affects the stability of biochar. Increased burn time result in biochars with greater C content and higher stability. Increased stability increases the refractory index of the biochar meaning that biochar will degrade much slower than other chars (Downie et al., 2009; Kazemi Shariat Panahi et al., 2020). Biochars produced <350 °C, have a C content of ~45% C meaning lower aromaticity, making it less stable over time than biochars produced 500-800 °C which have a C upwards of 60% meaning biochar is more chemically inert making it suitable for long term C storage (Kazemi Shariat Panahi et al., 2020).

Figure 2.3. Cell 1 taken from Cell 1 intermediate Location control dose.

Figure 2.4. Cell 2 taken from Cell 1.

Figure 2.5. Cell 1: Dry Location. Half dose of biochar applied.

Figure 2.6. Cell 3: Wet Location. Full dose of biochar.

Figure 2.7. Cell 2: Intermediate Location. Full dose of biochar applied.

Table 2.2. Chemical composition of biochar used within this trial.

	Carbon(%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%)
Biochar	74.74	3.08	0.062	14.21

3. Effects of biochar on water quality of a lowland raised bog

3.1. Introduction

As was outlined in chapter 1, peatlands are globally important carbon stores. However, the rate of anthropogenic climate change is faster than the rate at which peatlands can sequester and store C. Many years of peatland exploitation and degradation mean peatlands need to be enhanced to improve C storage. Biochar is a refractory form of carbon capable of storing carbon for many years its ability to maintain its structural and chemical properties makes it a suitable material to enhance the carbon sequestration of peatlands. However, the effect that biochar has on water quality within peatland environments was not known.

This chapter assesses the effect of biochar application to a lowland raised bog on water quality.

3.2. Water quality methods

3.2.1 Water quality field sampling methods

Dipwells were installed vertically into the peat to an approximate depth of 80 cm in all 27 experimental plots. Water table depths were calculated, by measuring the depth of water from the top of the dipwell to the surface of the water, from which the height of the top of the well above the soil surface was subtracted to account for any shrinking or swelling of the peat soil. Depth to water table was measured prior to soil water samples being collected, as to avoid any error in the depth measurement post sampling.

Soil water was sampled from the dipwell located within each plot. For water quality analysis, 50 ml samples (two samples per plot) were extracted each month from February 2022 to May 2023. A sample of 50 ml was collected by dipping a stick with a 50 ml sample pot attached to the end, into a dipwell. The first sample was discarded and the subsequent two samples were retained for analysis.

3.2.2. Water quality analysis

Samples were stored in a fridge at 4°C after collection from the field. Samples were filtered through 0.45 μm cellulose-acetate syringe filters and pH, conductivity and absorbance measured the day after they were gathered in the field. Anion analysis by ion chromatography (IC) was carried out in batches every couple of months on filtered samples. Anions of nitrate (NO_3^-), orthophosphate (PO_4^{3-}), and sulphate (SO_4^{2-}) were analysed. Anions were analysed in order to determine the nutrient content of the peat soil water, indicating whether the application of biochar may have brought nutrients onto the peatland. Cation analysis performed by inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out after final field samples were collected in May 2023. Cations of iron (Fe), were analysed to see if the application of biochar changed the supply of TEAs within the peatland. Analysis for dissolved organic carbon (DOC) was carried out in June 2022 and June 2023 on all filtered samples collected up to these dates. All samples remained at 4°C in the dark when not being analysed.

3.2.2.1. pH

Unfiltered samples were first analysed for pH using an electrode method (HI-9025 Hanna Instruments). This instrument had been previously calibrated to pH 4 and pH 7. Readings taken have an assured accuracy of ± 0.01pH. The calibration process was repeated and pH recorded for each sample obtained each month.

3.2.2.2 Conductivity

Conductivity was analysed on unfiltered samples using an electrode method (HI-9033 Hanna Instruments). The conductivity probe was previously calibrated to ensure an accurate measure to a guaranteed accuracy of 1 µs/cm. This process was repeated and values recorded for all samples.

3.2.2.3. Absorbance

Absorbance analysis was determined at 400 nm (Abs400) on filtered samples. This wavelength is commonly used by water companies for watercolour readings of freshwater samples (e.g. Armstrong et al., 2010). The absorbance was measured on a UV-Vis spectrometry machine. A blank was measured after every third sample to prevent analytical drift using distilled: de-ionised water was used as the blank.

3.2.2.4. Dissolved organic carbon (DOC)

The method used for determining DOC is adapted from a method used for the examination of water and wastewater (Eaton et al., 1995). DOC determines the value of organic carbon (OC) in a given sample able to pass through a ≤ 0.45 µm filter and is useful for showing levels of water quality. The DOC content was determined by calculating the difference between the total carbon and inorganic carbon content within each sample. The instrument used was the ShimadzuTOC-L. Standards used were 0, 1.0, 5.0, 10.0, 30.0, 50.0 mg/l from potassium hydrogen phthalate.

3.2.2.5. Anion analysis

Anion concentrations of Nitrate (NO_3^-), orthophosphate (PO_4^{3-}), and sulphate (SO_4^{2-}), were measured using ion chromatography (Metrohm 761 Compact IC connected to an 813 Compact Auto-sampler). The instrument used was the Thermo - ICS6000, standard solution concentrations used are in Table 3.1.

Table. 3.1. Standard solutions concentrations used in determining anion concentration.

Anion	Calibration standards (mg/l)
NO_3^-	0.5, 1.0, 2.0, 4.0, 8.0, 12.0, 16.0, 20.0
SO_4^{2-}	0.75, 1.5,3.0, 6.0, 12.0, 18.0, 24.0, 30.0
PO_4^{3-}	0.25, 0.5,1.0, 2.0, 4.0, 6.0, 8.0, 10.0

3.2.2.6. Inductively coupled plasma - optical emission spectroscopy (ICP-OES)

Analysis by ICP-OES was carried out on a Thermo Scientific ICAP 6000 series ICP-OES spectrometer. Analysis was performed for iron (Fe). Standard concentrations and appropriate wavelengths for the analysis were chosen based on previous predictions of expected concentrations of metals within peat porewater. Due to the high concentration of DOC, all samples were diluted before analysis. Blanks containing diluted stock solution and no soil water were run through the ICP-OES to ensure the blank was producing the expected wavelength as to reduce error when running the soil water samples.

For the DOC, anion, and ICP-OES analyses, not all samples from each month were analysed. The samples (n=27) from all 27 plots were analysed for February 2022. For August 2022 and September 2022, all collected samples were analysed, however, no complete sets of samples could be collected because some dipwells dried out during these months. For sampling in all other months, not all available samples were analysed as means to save cost. However, in these months the samples were selected so as to ensure the combination of the factors was covered but just in triplicate. Samples selected in this way were then included in anion, ICP-OES and DOC analysis. This approach maximised statistical and multivariate information within the available resources.

3.3 Statistical analysis of water quality

3.3.1 Analysis of variance (ANOVA) and Covariance (ANCOVA)

Experiment design of this project was such that different factors could be compared. Analysis of variance (ANOVA) was used to assess the significance of all four factors within the experimental design (Cell, Location, Treatment and Month). The ANOVA was performed including all factors and the two-way interactions of the factors.

As this study was looking at the effect of treatment with biochar. ANOVA of one way factor interaction showed whether Treatment caused a significant difference between control and treated plots for any water quality. Treatment with biochar over time was also assessed. ANOVA of two way interactions showed whether the Month*Treatment interaction was significant i.e. whether Treatment with biochar caused a significant effect and whether this effect persisted or diminished with time. In addition, water quality parameters were included as covariates where appropriate, in which cases the analysis was performed first without and then with their inclusion. Including covariates allowed the importance of the covariate in explaining the impact of a factor to be tested. As this study looked at Treatment as a factor and the Month*Treatment interaction, other factors and interactions are not covered in this thesis. Treatment and the Month*Treatment interaction are the most valuable factor and interaction in understanding the impact of biochar addition on peatland soil water quality.

Both relative and absolute data were used during ANOVA and ANCOVA analysis. Relative data were used to demonstrate change relative to control, pre-treatment data. Absolute data were used to provide contextual application to wider literature.

ANOVA assumes the data being analysed are normally distributed. Prior to any ANVOA the data were thus assessed for normality using the Anderson-Darling test (Anderson and Darling, 1952). If data were found to be non-normal the data were log-transformed and re-tested: further transformation – in this further transformation did not prove necessary. Significance was tested at the 95% level (> 95% (0.95) probability of being different from zero: > 5% probability of being zero) unless otherwise stated.

Post hoc analysis was performed using the Tukey test and marginal means to establish the significance between factor levels, and interaction terms. Marginal means are means extracted from one way ANOVA to represent the response factors of water quality determinants, provided to 95% confidence interval unless other stated.

R-squared (R^2) is a statistical measure produced during ANOVA, that represents the proportion of the variance for a dependent variable. R^2 values range from 0 to 1, an R^2 value of 1 means that 100% of the determinant can be explained by that one factor. Values between 0 but less than 1 can be explained by more than one factor. Eta-squared (η^2) measures the proportion of total variation of a determinant that can be accounted for by a dependent variable in one way ANOVA.

3.3. Water quality results: Water table, pH, conductivity, DOC, absorbance, anion and ICP-OES.

Table 3.3. Summary water quality results – arithmetic mean and range.

Determinand	No. data points	Full dose mean	Half dose mean	Control dose mean	Overall mean	Full dose range	Half dose range	Control dose range	Overall range
Absolute water table (mm)	462	0.75	0.75	0.78	0.76	0.1 - 1.2	0.1 - 1.1	0.2 - 1.8	0.1 - 1.8
Relative water table (mm)	462	0.75	0.75	0.78	0.76	0.1 - 1.2	0.1 - 1.1	0.2 - 1.8	0.1 - 1.8
Absolute pH	349	4.19	4.12	4.15	4.15	3.29 - 5.45	3.07 - 6.18	3.22 - 6.88	3.07 - 6.68
Relative pH	349	1.24	1.20	1.20	1.21	0.94 - 1.65	0.82 - 1.95	0.93 - 1.95	0.82 - 1.95
Absolute conductivity	349	109.79	121.75	105.62	112.44	32.8 to 240	63.3 to 312	40 - 310	32.8 - 312
Relative conductivity	349	1.08	1.20	1.07	1.11	0.33 - 2.28	0.51 - 2.5	0.46 - 2.44	0.33 - 2.50
Absolute absorbance	334	0.57	0.68	0.44	0.58	0.05 - 1.31	0.14 - 1.57	0.11 - 1.41	0.05 - 1.57
Relative absorbance	334	0.60	0.71	0.45	0.582	0.114 - 1.214	0.144 - 1.571	0.106 - 1.412	0.106 - 1.571
Absolute DOC (mg/l)	161	103.9	115.6	91.00	103.6	8.3 - 321.3	23.7 - 267.2	22.5 - 283.7	8.3 - 321.3
Relative DOC (mg/l)	161	0.72	0.97	0.76	0.82	0.25 - 1.87	0.24 - 3.38	0.13 - 2.67	0.13 - 3.38
Absolute Nitrate (mg N/l)	151	0.03	0.03	0.02	0.03	0.01 - 0.25	0.01 - 0.48	0.01 - 0.81	0.01 - 0.48
Relative Nitrate (mg N/l)	151	0.27	0.22	0.07	0.19	0.00 - 4.06	0.00 - 5.18	0.00 - 0.81	0.00 - 5.18
Absolute Phosphate (mg P/l)	151	0.14	0.26	0.19	0.19	0 - 1.26	0.00 - 5.18	0.00 - 0.86	0.00 - 5.18
Relative Phosphate (mg P/l)	151	0.18	0.17	0.20	0.18	0.04 - 0.86	0.04 - 1.00	0.04 - 1.23	0.04 - 1.23
Absolute Iron (mg Fe/l)	149	3.00	2.10	1.83	2.27	0.13 - 20.31	0.13 - 13.15	0.12 - 13.22	0.12 - 20.31
Relative Iron (mg Fe/l)	149	7.92	5.19	7.00	6.67	0.28 - 60.19	0.27 - 35.73	0.35 - 73.04	0.27 - 73.04

Absolute Sulphate (mg S/l)	151	1.92	1.49	0.80	1.44	0.11 - 13.75	0.08 - 7.18	0.10 - 7.45	0.08 - 13.75
Relative Sulphate (mg S/l)	151	3.2	3.86	2.34	3.21	0.18 - 24.9	0.17 - 30.8	0.15 - 8.5	0.15 - 30.8

Table 3.2. Summary of ANOVA results - percentage importance of original variance of relative water quality determinands. ***Significant factor or interaction at $p > 0.05$.**

Determinand	Month	Cell	Location	Treatment	Month*Treatment	Month*Location	Month*Cell	Treatment*Location	Treatment*Cell	Location*Cell	R^2
Water table	**14***	**3***	**2***	2	28	**28***	28	4	**4***	**4***	0.770
pH	**23***	**7***	**5***	2	9	**26***	**27***	**8***	**7***	**7***	0.603
Conductivity	**14***	**5***	**6***	**2***	**26***	**28***	25	6	6	23	0.733
DOC	**13***	2	2	2	24	25	23	4	4	4	0.694
Absorbance	**14***	**6***	**4***	**2***	26	**26***	**24***	5	**6***	**5***	0.652
Nitrate	**13***	**3***	**3***	**2***	**24***	**24***	**14***	4	**4***	2	0.986
Phosphate	**11***	**2***	1	2	**22***	**25***	**18***	4	4	4	0.978
Sulphate	**10***	**3***	2	4	19	20	**17***	4	4	4	0.866
Iron	12	2	**2***	2	24	23	**22***	4	4	4	0.861

Table 3.4. Summary of ANCOVA results - percentage importance of original variance of relative water quality determinands. *Significant factor or interaction at p > 0.05.

Determinand	**Month**	**Cell**	**Location**	**Treatment**	**Relative water table**	**Month*Treatment**	**Month*Location**	**Month*Cell**	**Treatment*Location**	**Treatment*Cell**	**Location*Cell**	**R^2**
pH	**14***	**2***	**2**	**2***	**1***	25	**24***	**24***	**4**	**4***	**4**	0.603
Conductivity	**14***	**2***	**2***	**2***	1	24	**24***	23	4	4	**4***	0.698
Absorbance	**14***	**2***	2	**2***	**1***	25	**24***	**23***	4	**4***	4	0.698
DOC	**14***	2	2	**2***	**1***	25	**24***	**23***	4	**4***	4	0.670
Nitrate	**13***	**2***	**2***	**2***	1	**23***	**24***	**12***	**4***	4	**3***	0.996
Phosphate	**13***	**2***	1	**2***	**1***	**19***	**13***	**12***	2	**4***	**8***	0.998
Sulphate	**13***	**2***	2	2	1	**23***	**23***	**20***	**4***	4	4	0.929
Iron	11	2	1	2	1	18	10	11	2	3	1	0.881

3.3.1. Water table

There were 462 water table data points of a possible 548. Prior to analysis the Anderson Darling test was performed and data were found to be normally distributed. The ANOVA of relative water table data showed that Treatment was not significant at $p > 0.05$, nor was the Month*Treatment interaction (Table 3.3).

The Location factor used within this study was chosen based on plots not being hydrologically connected. The lack of a significant Treatment factor and Month*Treatment interaction confirms the Location factor, that plots were not hydrologically connected.

3.3.2. pH

There were 349 measurements of absolute pH compared to a possible 405. Mean absolute pH across all Treatment levels was 4.15 ± 0.06 (Table 3.2). Prior to ANOVA the Anderson Darling test was performed and data were found to be normally distributed. The ANOVA of relative pH showed Treatment was not a significant factor at $p > 0.05$. The Month*Treatment interaction was also not significant at $p > 0.05$ (Table 3.3).

The ANCOVA with relative water table as a covariate showed an increase in the R^2 value by 0.022 ± 0.06. Relative water table was significant when included as a covariate in the analysis. With the addition of relative water table as a covariate, Treatment became a significant factor: Month*Treatment interaction remained not significant (Table 3.4)

The post hoc Tukey tests showed that there were significant differences between the half- and full-dose treatments, and between the full-dose and the control treatments, but not between the half-doe and control treatments.

Given the alkali pH of biochar we expected, *a priori*, for biochar to significantly increase the pH of peatland soil water: this was not observed. When differences in water table were allowed for, there was a small but significant effect due to biochar Treatment. There was an increase of 0.005 in Treatment effect size when relative water table differences were considered (Figure 3.1).

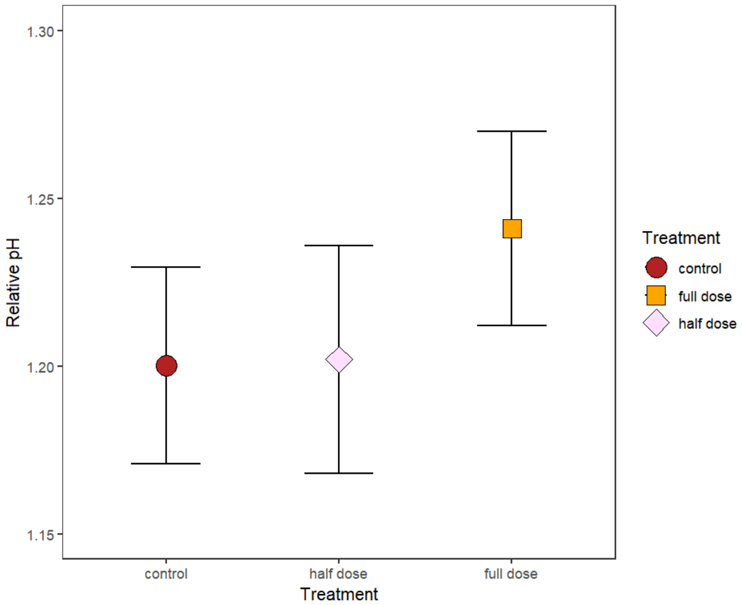

Figure 3.1. Main effects plot of Treatment of peat soil water pH relative to pre treatment levels. The datapoint is the marginal means and the whiskers are the 95% confidence interval.

3.3.3. Conductivity

Given the low conductivity typically measured in peat soil water (Walter et al., 2015), it was expected, *a priori*, for conductivity to significantly increase due to possible contamination from biochar.

There were 349 conductivity data points of a possible 405. Mean absolute conductivity across Treatment levels was 112.45 ± 0.05 μS/cm (Table 3.2). Prior to analysis, the Anderson Darling test was performed. Data were not normally distributed, and therefore the data were log transformed and re-tested with no further transformation necessary. The ANOVA of relative conductivity data showed Treatment was a significant factor at $p < 0.05$, and explained 7% of the original variance (Table 3.3). The difference between control Treatment and half dose Treatment was an increase of 16.13 ± 0.05 μS/cm; between the control and full dose was and increase 4.17 ± 0.05 μS/cm and between half dose and full dose was a decrease of 11.96 ± 0.05 μS/cm. Month*Treatment interaction was significant at $p < 0.05$ and explained 26% of the original variance in the dataset (Table 3.3; Figure 3.2).

ANCOVA with relative water table as a covariate showed relative water table was not significant. With water table as a covariate Treatment remained significant. Month*Treatment interaction became not significant, the effect size increased by 0.001% (Table 3.4). Therefore, the Treatment effect over time (the Month*Treatment interaction) was explained by changes in water table. The impact of the water on soil water conductivity appears to be in the summer months when water table were very low. There was no observed significant difference in soil water conductivity over time between the treatments that persisted after the summer so implying no diminishing or increasing impact of the biochar addition.

Post hoc Tukey test showed a statistical difference between all the combinations of the Treatment factor levels. With the inclusion of water table as a covariate the difference between relative full dose and control was 3 ± 0.02 μS/cm the difference between half-dose and control was 12.64 ± 0.02 μS/cm and the difference between half- and full-dose was 9.28 ± 0.02 μS/cm (Figure 3.2).

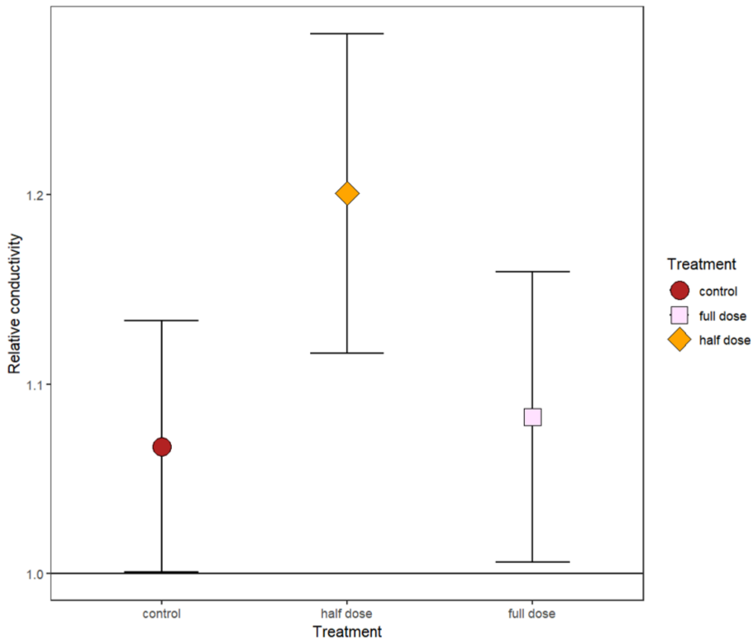

Figure 3.2. Main effects plot of Treatment of peat soil water conductivity relative to pre-treatment levels. The datapoint is the marginal means and the whiskers are the 95% confidence. interval.

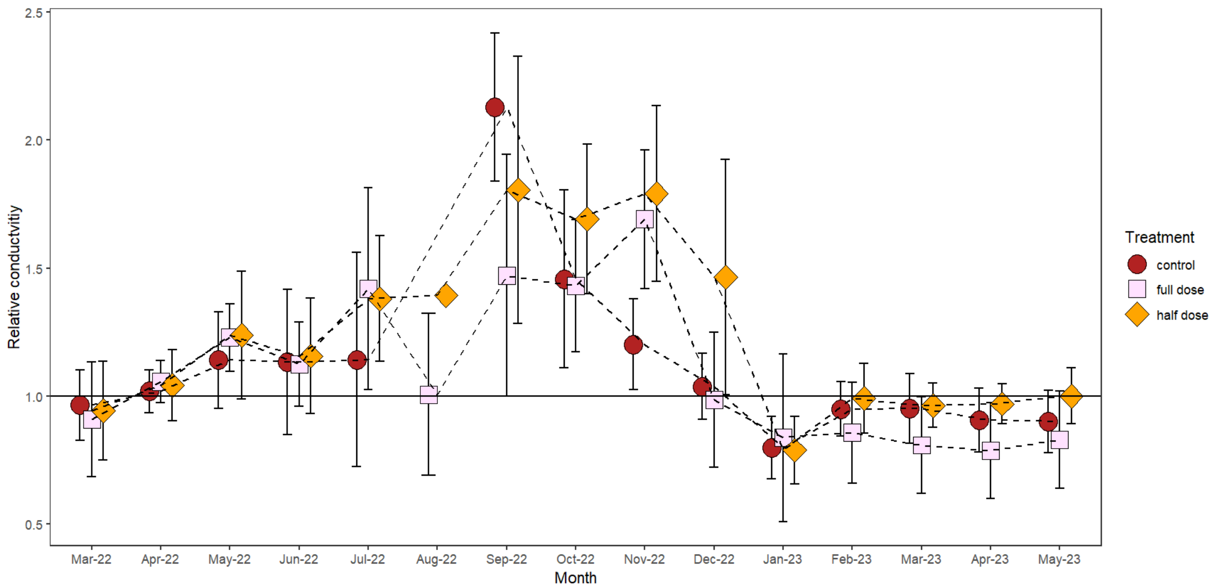

*Figure 3.3. Main effects plot of the Month*Treatment interaction of peat soil water conductivity. The datapoint is the marginal means and the whiskers are the 95% confidence interval. The plotted points are offset around the Month factor levels to ensure visibility.*

3.3.4. Absorbance

There were 334 absolute absorbance readings of a possible 405. The overall mean of absolute absorbance was 0.582 ± 0.03 (Table 3.2). Prior to analysis the Anderson Darling test was performed and data were not normally distributed and were therefore log transformed – no further transformation proved necessary. The ANOVA of relative absorbance data showed Treatment was significant at $p < 0.05$ (Table 3.3, Figure 3.4). The absorbance on the half dose Treatment was 26.5% higher than on the control Treatment. The absorbance of the full dose was 15% greater than of the control treatment; and the absorbance of the half dose was 11.1% greater than that of the full dose treatment. However, the post hoc comparison of the absorbance between the Treatment shows that there was a significant differences between both the half dose and the control; and between the full dose and the control. However, there was no significant difference between the half dose and full dose. The Month*Treatment interaction was not significant at $p > 0.05$.

ANCOVA with relative water table as a covariate showed water table was significant when included as a covariate. The pattern of significance among determinants did not change, i.e. Treatment remained significant and Month*Treatment remained insignificant (Table 3.4). Post hoc Tukey test shows that there was a statistical difference between the half-dose and control of 0.37± 0.03, and full dose and control of 0.38 ± 0.03 but half- and full- dose was not statistically different.

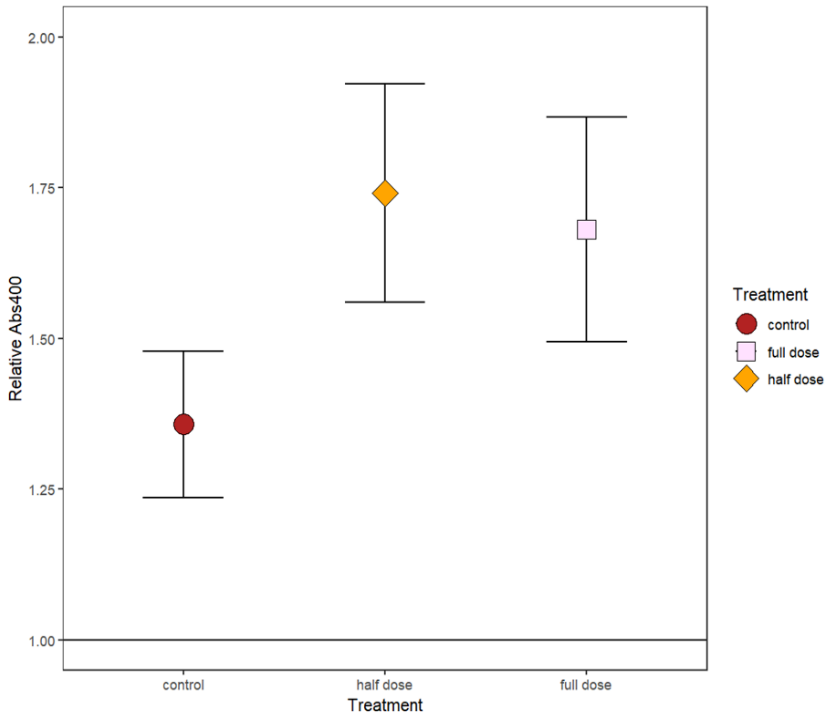

Figure 3.4. Main effects plot of Treatment of peat soil water absorbance relative to pre-treatment levels. The datapoint is the marginal means and the whiskers are the 95% confidence interval.

3.3.5. Dissolved organic carbon (DOC)

There were 161 DOC concentration measurements. The mean absolute DOC across Treatment levels was 103.6 ± 10.2 mg C/l (Table 3.2). Prior to analysis the Anderson darling test was performed. Data were not normally distributed, and therefore, the data were log transformed. The ANOVA of relative DOC showed that neither Treatment nor the Month*Treatment interaction were significant at $p > 0.05$ (Table 3.3).

When relative water table was included in ANCOVA then Treatment became significant (Figure 3.5), but the Month*Treatment interaction remained insignificant (Table 3.4). The relative water table as a covariate explained 1% of the original variance. When water table was included as a covariate effect size of Treatment factor increased by 0.5%. Post hoc Tukey test shows that there was a significant difference between the half-dose and control and full dose and control, but that the difference between the half- and the full- dose was insignificant.

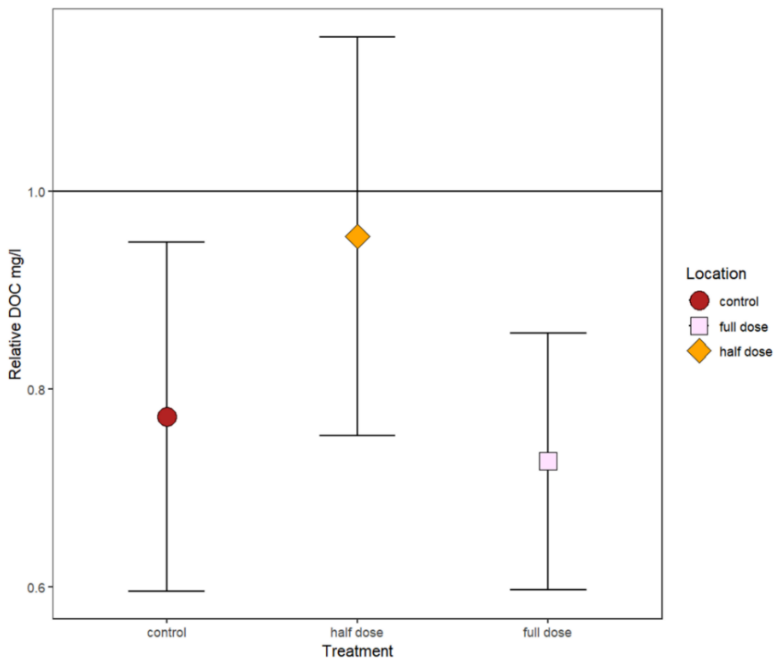

Figure 3.5. Main effects plot of Treatment of peat soil water DOC concentration relative to pre-treatment levels. The datapoint is the marginal means and the whiskers are the 95% confidence interval.

3.3.6. Nitrate

There were 153 nitrate concentration measurements, the mean absolute nitrate concentration across all Treatment levels was 0.19 ± 0.01 mg N/l (Table 3.2).

Prior to analysis, the Anderson Darling test was performed and data were found not to be normally distributed, so were log transformed and retested with no further transformation proving necessary. The ANOVA performed in the relative nitrate concentration data showed Treatment was significant at $p < 0.05$ (Figure 3.7) and explained 24% of the original variance (Table 3.3). The difference between control Treatment and half dose Treatment was 0.15 ± 0.01 mg N/l. Control and full dose was 0.2 ± 0.01 mg N/l and between half dose and full dose was 0.05 ± 0.01 mg N/l (Figure 3.6). Month*Treatment interaction of relative nitrate concentration data was significant at $p > 0.05$ and explained 27% effect of original variance (Table 3.3) (Figure 3.7).

The ANCOVA with relative water table as a covariate showed an increase in the R^2 value by 0.01. Relative water table was not significant when included as a covariate in the analysis. With the addition of relative water table as a covariate, the significance pattern did not change - Treatment and Month*Treatment remained significant (Table 3.4). The post hoc Tukey test showed that half- and full-dose treatments were statistically different as well as half-dose and control. Full-dose and control were not statistically different.

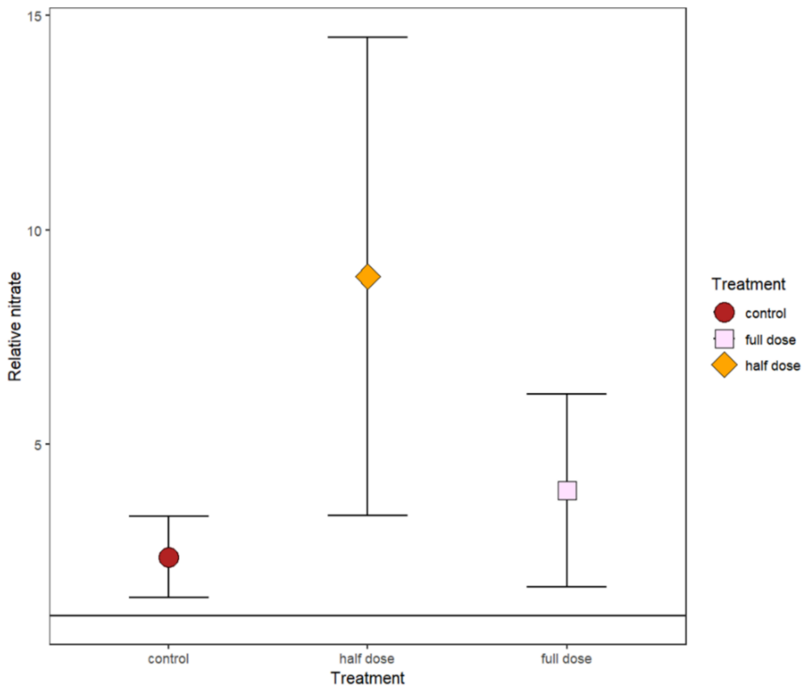

Figure 3.6. Main effects plot of Treatment of peat soil water nitrate concentration relative to pre-treatment levels. The datapoint is the marginal means and the whiskers are the 95% confidence interval.

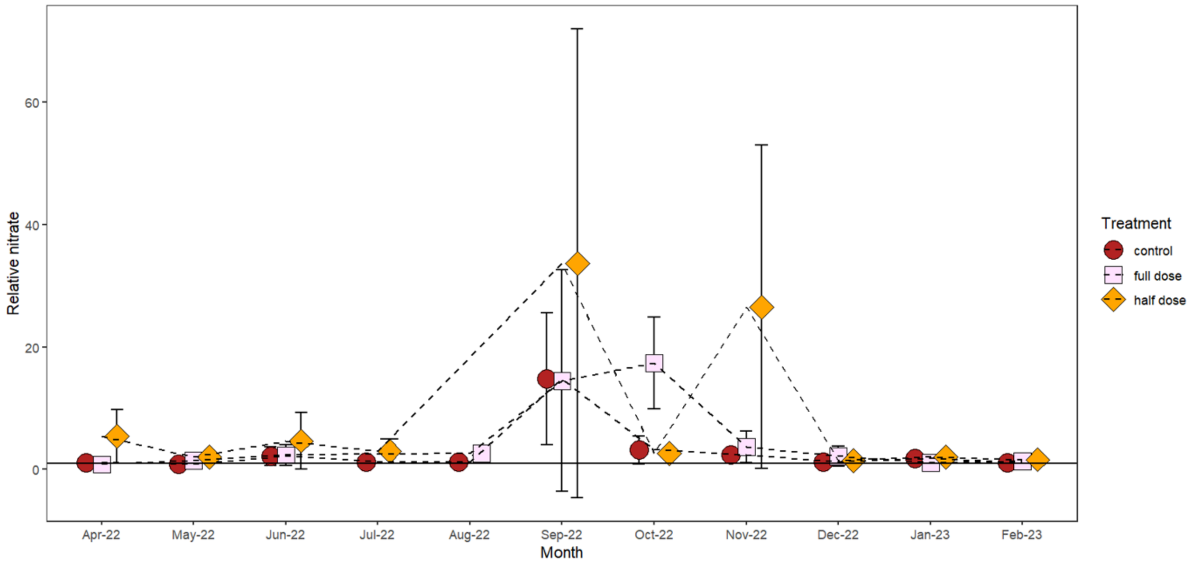

*Figure 3.7. Main effects plot of the Month*Treatment interaction of peat soil water nitrate. The datapoint is the marginal means and the whiskers are the 95% confidence interval. The plotted points are offset around the Month factor levels to ensure visibility.*

3.3.7. Phosphate

There were 151 phosphate concentration data points, the mean absolute phosphate concentration across all Treatment levels was 0.18 ± 0.07 mg P/l (Table 3.2).

Prior to analysis, the Anderson Darling test was performed and data were found to be normally distributed. The ANOVA of absolute phosphate concentration data showed Treatment was not significant at $p < 0.05$, but Month*Treatment interaction of absolute phosphate concentration data was significant at $p > 0.05$ and explained 22% of the original variance (Table 3.3, Figure 3.9). The difference between control Treatment and half dose Treatment was -0.03 ± 0.07 mg P/l. Control and full dose Treatments was -0.02 ± 0.07 mg P/l; and between half dose and full dose treatments was 0.01 ± 0.07 mg P/l.

The ANCOVA with relative water table as a covariate showed an increase in the R^2 value by 0.02. Relative water table was significant when included as a covariate in the analysis. With the addition of relative water table as a covariate Treatment became significant (Figure 3.8), and Month*Treatment remained significant (Figure 3.9) (Table 3.4). Post hoc Tukey test shows, a statistical difference between all the combinations of the Treatment factor levels.

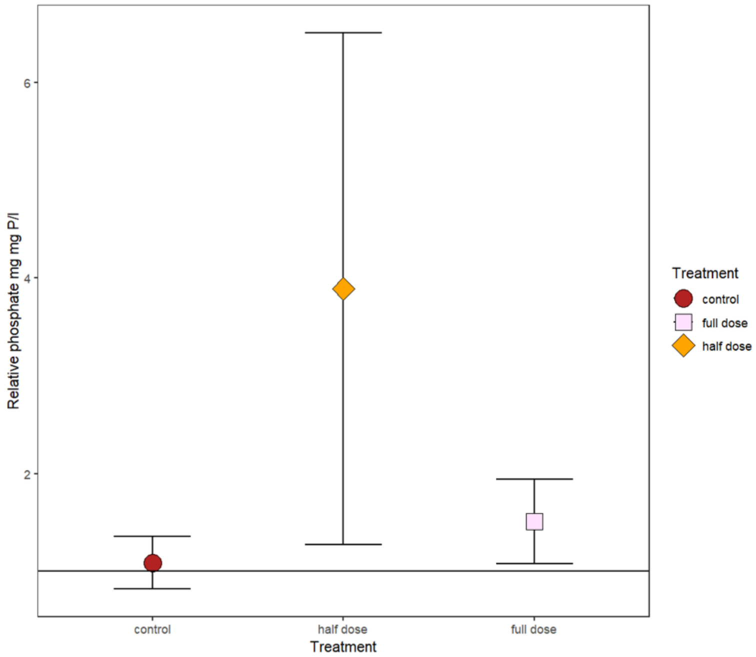

Figure 3.8. Main effects plot of Treatment of peat soil water phosphate concentrations relative to pre-treatment levels. The datapoint is the marginal means and the whiskers are the 95% confidence interval.

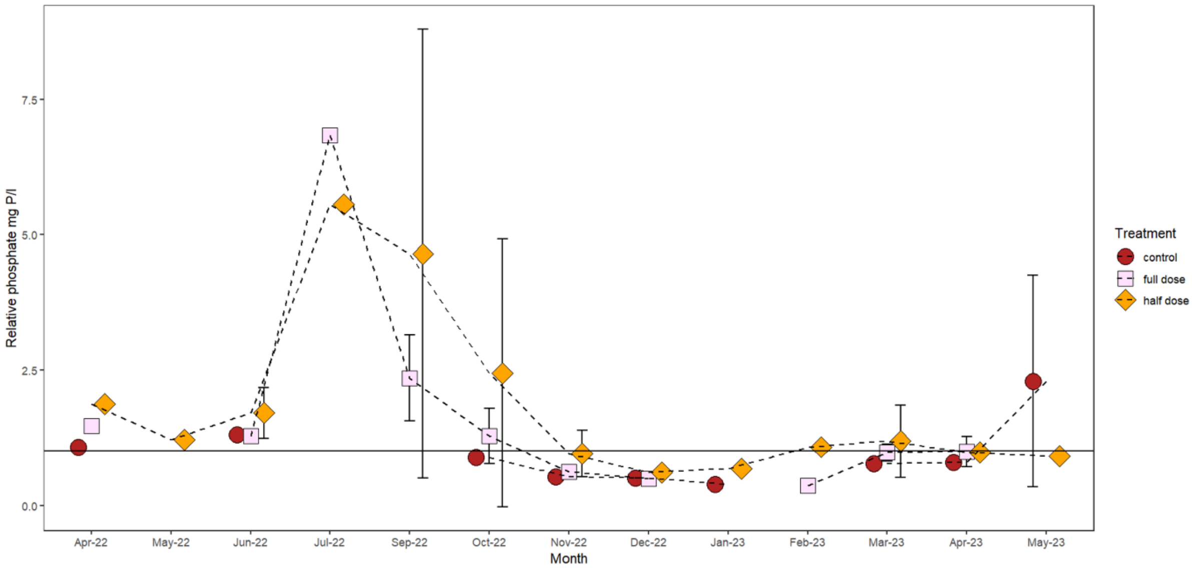

*Figure 3.9. Main effects plot of the Month*Treatment interaction of peat soil water phosphate. The datapoint is the marginal means and the whiskers are the 95% confidence interval. The plotted points are offset around the Month factor levels to ensure visibility.*

3.3.8. Iron

There were 149 Fe concentration data points, the mean absolute Fe concentration across Treatment levels was 6.67 ± 0.58 mg/l (Table 3.2).

Prior to analysis, the Anderson Darling test was performed, data were not normally distributed and therefore the data were log transformed, and no further transformation proved necessary. The ANOVA of relative Fe data showed Treatment and the Month*Treatment interaction were not significant at $p > 0.05$ (Table 3.3).

The ANCOVA with relative water table as a covariate showed an increase in the R^2 value by 0.02. Relative water table was not significant when included as a covariate in the analysis. The pattern of significance did not change with the addition of relative water table as a covariate, Treatment and Month*Treatment remained insignificant. Post hoc Tukey test showed no statistical difference between any Treatment combinations (Table 3.4).

3.3.8. Sulphate

There were 123 sulphate concentration data, the mean absolute sulphate concentration across Treatment levels was 3.21 ± 0.34 mg S/l (Table 3.2). Prior to analysis, the Anderson Darling test was performed, and data were found to be normally distributed. The ANOVA of relative sulphate data showed Treatment was not significant at $p > 0.05$, Month*Treatment interaction was also not significant at $p > 0.05$ (Table 3.3).

The ANCOVA with relative water table as a covariate showed an increase in the R^2 value by 0.06. Relative water table was not significant when included as a covariate in the analysis. The pattern of significance did not change with the addition of relative water table as a covariate, Treatment and Month*Treatment remained insignificant (Table 3.4). Post hoc Tukey tests showed no statistical difference between all the combinations of the Treatment factor levels.

3.4 Water quality discussion

3.4.1. pH

The biochar used in this study was alkali like most biochars (Lehmann and Joseph, 2015), while in contrast peat soils are typically acidic (e.g., Syifa et al., 2019). It was, therefore, a cause for concern that the addition of biochar to the surface of a peatland could significantly increase the pH of the soil water. Increased soil pH might in turn impact the peatlands functionality and biota. However, the addition of alkali biochar to the study plots in this experiment led to no observed changes. There was no significant difference in peat soil water pH due to the Treatment. However, when relative water table was included as a covariate the Treatment factor became significant, having an effect size which explained 2% of the original variance. Suggesting the changes in water table were masking the effect biochar had on pH of soil water. Though treatment with biochar significantly increased pH, the magnitude of change was a small percentage of the values observed for the control. A 2% effect size, although significant, is relatively small and therefore unlikely to produce any tangible difference nor affect the function of a peatland.

Syifa et al. (2019) state the natural range of peat soil water pH is between 3.7 and 5.2. Boothroyd et al. (2012) state the peat soil water pH at Moor House ranged from 4.3 to 4.6. Novak et al. (2005) reported the pH of soil water at Thorne Moors as 4.6 ± 0.8. pH at half- and full-dose Treatment plots at Hatfield ranged from 3.1 to 6.2, and the average soil water pH of half- and full-dose plots was 4.15 ± 0.07. Even with the application of biochar the mean pH was still within the natural range of peatlands and within the range of soil water pH at Thorne Moors and Moor House.

Previous peatland management have monitored the effects of management techniques on soil water pH. Managed burning is arguably the most analogue comparison to biochar application, as there is actively charred biomass left on the surface of the peatland (Clay and Worrall, 2011). A prescribed burn management study by Worrall et al. (2007) within Moor House NNR, reported a significant difference in soil water pH between burnt and unburnt plots, with burning decreasing the average pH and variability therein. The pH of unburnt plots ranged from 4.11 to 9.93 compared to manged burn plots, where pH ranged from 4.09 to 5.43. A revegetation study by Quassium et al. (2015) observed no significant change in pH after revegetation, reporting 5th to 95th percentile pH without revegetation of 3.6 to 5.9 comapred to 3.6 to 5.7 after revegetation. These two studies show peatland management may or may not cause a significant change in pH, likely depending on the type of management. However, the application of biochar is more likely to have similar effects on pH to that of burn management due to the nature of treatments. In this study, half- and full-dose Treatment plots ranged from 3.1 ± 0.06 to 6.2 ± 0.06, with a mean soil water pH on Treated plots of 4.15 ± 0.07 which was not significantly different from the mean control plots which had a mean pH of 4.15 ± 0.07. Compared to previous management studies we did not see a significant difference between Treated and non-Treated plots, nor was there any signifncnat difference over time.

3.4.2. Conductivity

Peat soil waters typically have relatively low conductivity often close to that of rainwater (Worrall et al., 2003). Applying biochar to the surface of a peatland was expected to be a potential source of solutes (e.g. Singh et al., 2018) and so increase the soil water conductivity. This study at Hatfield showed Treatment was significant, with and without differences in water table being considered, suggesting that biochar did significantly increase peat soil water conductivity. At Moor House the soil water conductivity was between 31.4 to 39.1 μS/cm: in this experiment at Hatfield the mean peat soil water conductivity at full dose Treatment was 109.8 μS/cm; 121.7 μS/cm at half dose Treatment: and 105.6 μS/cm for the control. The conductivity of the peat soil water on the control plots, where no biochar was applied would suggest typical conductivity at Hatfield Moors is greater than that of Moor House. One explanation of high conductivity at Hatfield, regardless of Treatment, is the water table balance of the site. The hydrology of Hatfield Moors is dominated by evaporation and there is only discharge in the months of January and February (Julian Small, pers. Comm). Thus, the soil water will undergo considerable concentration due to evaporation, hence high conductivity across all Treatments also. During months when water table was lowest it would be expected that conductivity would be highest due to the evaporation effect, which was observed at during this study at Hatfield.

Comparing the contrast of rainwater and soil water conductivity, it is possible to estimate a concentration factor of Hatfield. Conductivity concentration factor based on rainfall conductivity: 9.82 μS/cm, and known soil water conductivity of 39.1 μS/cm at Moor House and conductivity of soil water at Hatfield of 112.44 μS/cm, means the means the conductivity concentration factor at Hatfield is 3 ± 0.4 - the ratio of mean soil water conductivity observed at Hatfield compared to that observed for Moor House. Estimating a concentration factor based upon a conservative tracer such as conductivity will enable us to interpret whether other changes in non-conservative tracers are due to evaporative concentration rather than due to the impact of biochar.

Plotting conductivity against pH (Figure. 3.10) illustrates that high pH and high conductivity concentrations in soil water were independent of one another, further suggesting the cause of high conductivity of soil water at Hatfield, regardless of Treatment, was due to evaporation rather than other hydrological factors such as a ground water influence. If there had been a ground water influence it would have been expected that pH and conductivity would have covaried - this was not observed (Figure 3.10).

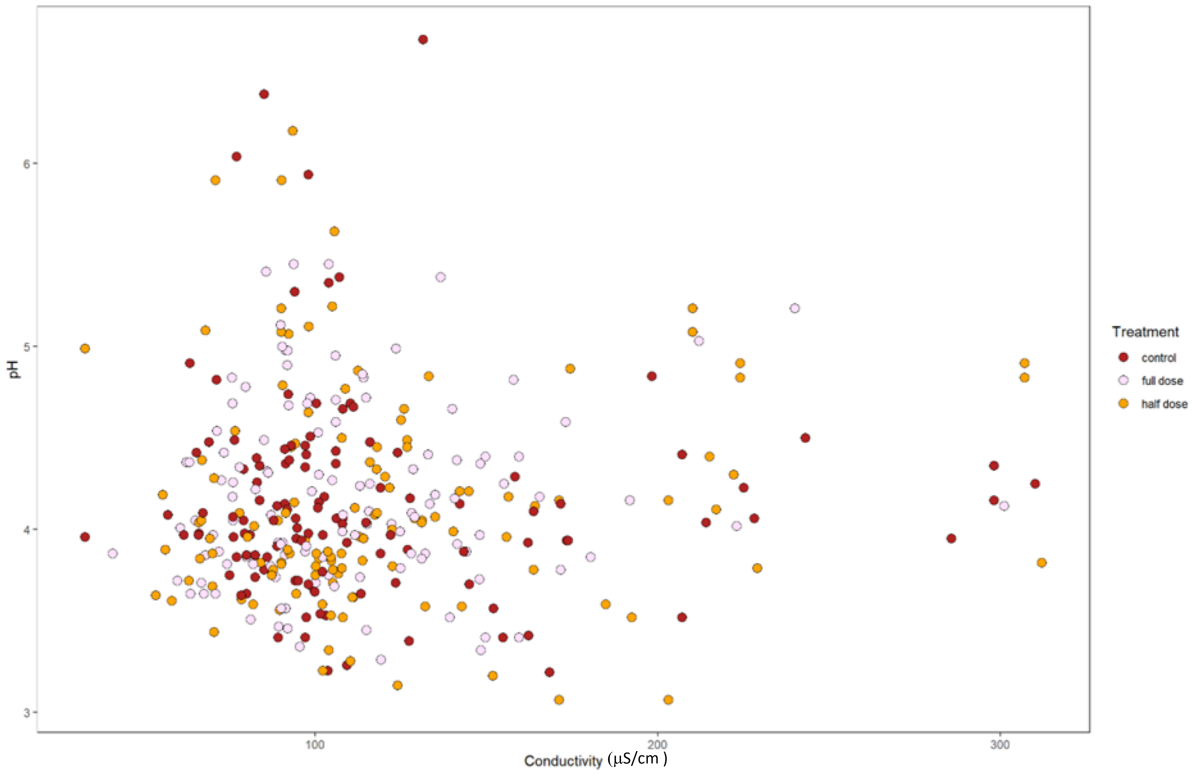

Figure 3.10. Plot of relative pH of peat soil water against conductivity of peat soil water.

3.4.3. Absorbance and DOC

As biochar is an adsorptive material, applying this to the surface of a peatland was expected to limit the movement of DOC within the peat. Additionally, as biochar itself is an organic material it may have DOC adsorbed to it or its own degradation may lead to dissolved organic matter (Lui et al., 2022).

Absorbance is often used as a proxy for DOC to assess its nature by examining the specific absorbance (Worrall et al., 2007). Measuring absorbance alongside DOC is a means of measuring the concentration and the composition of the DOC within the soil water. Previous studies have monitored the effect of peatland management on the concentration of DOC in soil water, and therefore, may suggest what the effect of biochar application on peatlands may have on DOC concentration. In a revegetation study across the Bleaklow Plateau which investigated the effects of revegetation on DOC concentration, Qassim et al. (2014) reported that the 5th to 95th percentile range prior to revegetation was 5.2 to 243 mg C/l. After revegetation the DOC concentration was 9.3 to 227 mg C/l, a significant increase from the control.

Worrall et al. (2013) observed the effect of vegetation cutting and burning on DOC concentration reporting that median DOC concentration prior to management was 142 mg C/l compared to 96 mg C/l after burning and 104 mg C/l after vegetation cutting. Qassim et al. (2014) reported an increase in

DOC concentration whereas Worrall et al. (2013) observed a decrease, suggesting the effect of peatland management on DOC concentration varies between management types. Here it would have been expected that burning would have the most similar effect on DOC concentration as biochar application. Compared to Worrall et al's. (2013) study of burning and cutting the 5^{th} to 95^{th} percentile range of half- and full-dose Treatment plots was 92.81 mg C/l compared to 96 mg C/l after burning and 104 mg C/l after revegetation suggesting the Treated plots at Hatfield are in the order of those observed by Worrall et al. (2013) after management.

This study has hypothesised that the high carbon content of the biochar and its associated high surface adsorption capacity mean that it could be a source of DOC to the soil water and so increase the absorbance of the soil water. Additionally, biochar has a high C content meaning it could be a source of DOC within the soil water increasing the DOC concentration of the soil water.

Despite DOC concentration being in the order of that reported in other peatland management studies, DOC concentration on half- and full- dose plots were significantly higher than the control plot concentrations. Plotting conductivity data from Hatfield against DOC (figure 3.11) suggests that the two act independently of one another. A concentration factor of 3 ± 0.4 suggests that evaporative concentration at Hatfield could explain a soil water DOC concentration of between 50.2 and 61.8 mg C/l, suggesting the DOC concentration at Hatfield was greater than expected regardless of Treatment.

Treatment and Treatment over time had no significant effect on the absorbance or DOC concentration of soil water. Average DOC at Hatfield was 103.6 ± 10.2 C mg/l, compared to a study at Moor House where reported DOC ranged from 17.5 to 21.3 mg C/l (Boothroyd et al., 2021). Overall DOC was higher than reported DOC for typical, unmanaged peatlands, but was in line with values of burnt and revegetated peatlands. As Treatment proved not to be significant and there was no relationship between absorbance and DOC, high DOC at Hatfield can be explained though evaporative concentration.

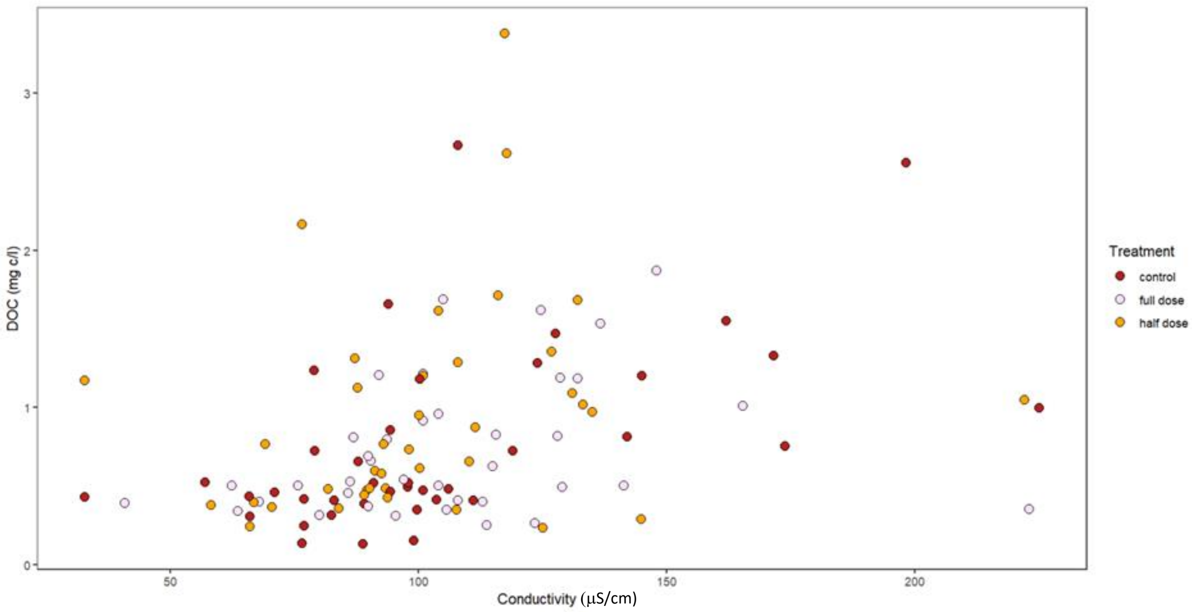

Figure 3.11. Plot of DOC against conductivity of peat soil water.

3.4.4. Nutrients

Peatlands are nutrient poor environments, and biochar is associated with the transport and modification of nutrient availability within soils (Joseph et al., 2021). It was thus expected that the addition of biochar would increase the nutrient concentration of soil water.

3.4.4.1. Nitrate

The results of this study suggest that biochar as a factor was significant in increasing the nitrate concentration of peat soil water in both relative and absolute nitrate concentration. The mean absolute nitrate concentration of half-and full-dose Treatment plots was 0.03 ± 0.01 mg N/l compared to the pre-treatment control plots.

The Month*Treatment interaction was significant, explaining 24% of the original variance, with and without covariates. Though water table was not significant when included as a covariate, the pattern in concentration of nitrate over the course of the study closely follows the seasonal water table. Highest concentrations of nitrate were observed at times of lowest water table levels, and an evaporation effect or ground water influence may explain this water table and nitrate concentration relationship. Even though when plotting nitrate concentration against conductivity shows high nitrate and high conductivity acted independently of one another (Figure 3.12). Despite this, due to the hydrological nature of Hatfield an evaporative effect would likely still be taking place during periods of low water table. Evaporation is the main way water leaves Hatfield. Hence nitrate concentrations will increase when the water table is lowest as evaporation is at its highest. Evaporative concentration would suggest nitrate concentrations at Hatfield would be on the order of 0.03 mg N/l rather than 0.19 mg N/l. However, this cannot be the case, as there was a difference in concentrations between control and Treatment plots, if evapotranspiration was the cause, then the change in nitrate concentration would be seen across Treatments including the control, but this was not observed.

As no explanation provided so far accounts for the significant increase in nitrate concentration between treated and control plots. A mean concentration of 0.27 mg N/l was observed at on full-dose plots, 0.22 mg N/l at half-dose plots and 0.07 at control plots. He et al. (2023) observed that nitrate in rainfall was adsorbed and then released after saturation of the biochar due to the absorptive nature of biochar. Essentially, biochar acted as a mechanism for nutrients to be held and then flushed through the peat soil water after rainfall, which could explain why a significant increase in nitrate concentration was observed at treated plots compared to control plots in my study

Gupta et al. (2016) found that applying biochar to a wetland significantly reduced the mean nitrate concentration from 5.1 mg/l to 2.4 mg/l. At Hatfield Treatment with biochar peatland, increased the nitrate concentration by 0.01 ± 0.01 mg/l. As evaporation is not the only cause it is possible that Hatfield has greater nitrate deposition than Moor House, for example. Equally at Hatfield there is small concentrations of nitrate within the soil pore water, possibly indicative of the TEA conditions.

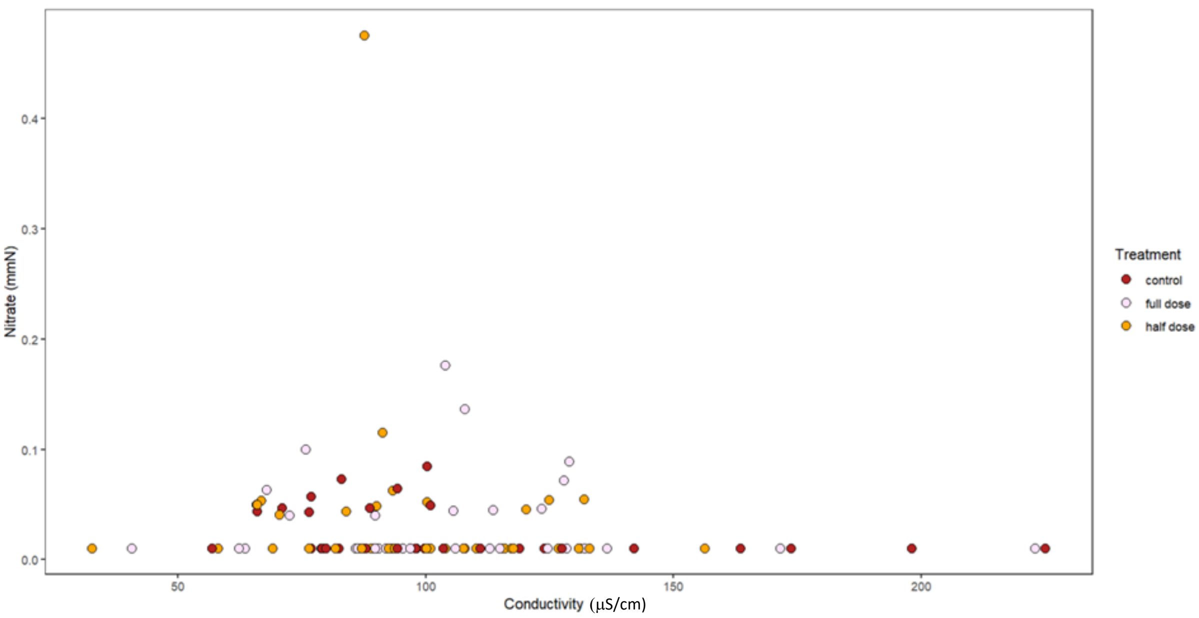

Figure 3.12. Plot of relative nitrate soil water concentration against conductivity of peat soil water.

3.4.4.2. Phosphate

In line with the expected increase in phosphate concentrations after the application of biochar due to the adsorptive nature of the biochar, a significant increase in phosphate concentration was observed due to Treatment and differences in water table. A prescribed burn management study by Worrall and Adamson (2008) found significantly reduced phosphorus concentration after burning. Due to the similarities of burning and biochar addition, and the adsorbate properties of biochar (e.g. Gupta et al., 2016) it might be expected that a decrease in phosphate concentration after biochar addition. Mean absolute phosphate concentration observed at Hatfield was 0.18 ± 0.07 mg P/l, higher concentration when compared to previous peatland and wetland management studies (e.g. Worrall and Adamson, 2008) As phosphate concentration was highest when the water table level was lowest, it may suggest that either groundwater or an evaporation effect was causing increased phosphate concentration. However, plotting phosphate against conductivity shows the two act independently of one another, if an evaporative effect was occurring it would be expected that to two would be simultaneous Figure 3.13). However, when water table and phosphate are plotted, it shows that when water table is lowest concentration of phosphate is highest.

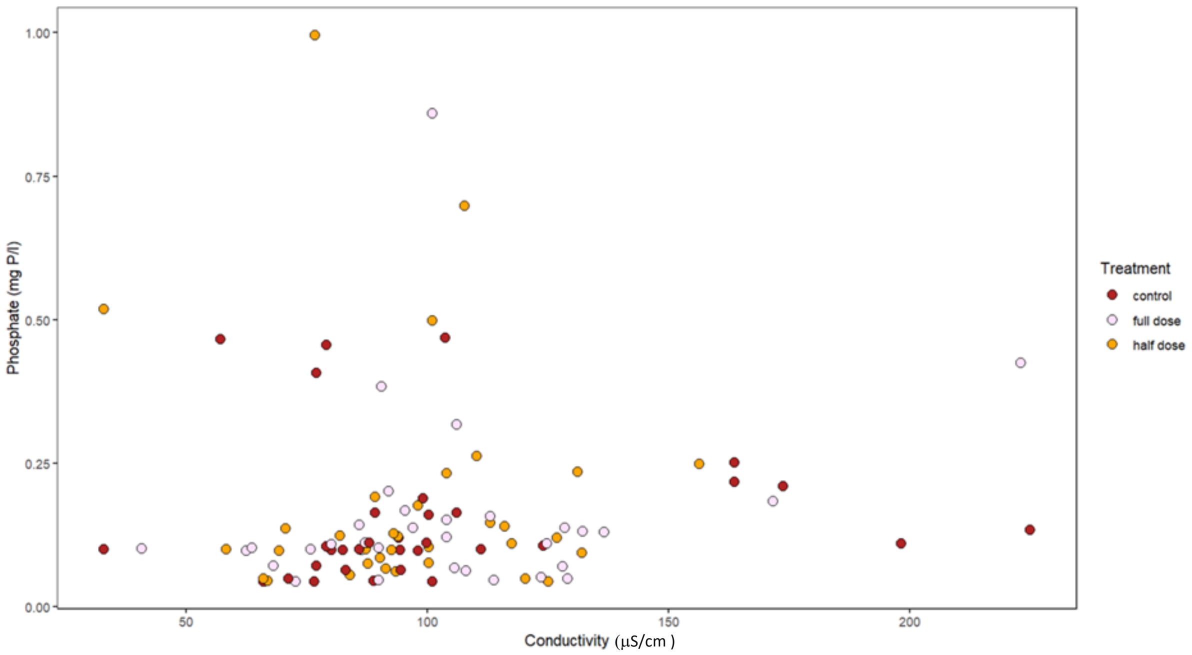

Figure 3.13. Plot of absolute phosphate soil water concentration against conductivity of peat soil water.

3.4.5. Terminal electron acceptors (TEA)

The balance of plant primary productivity and oxidation of organic matter maintains the existence of peatlands, an increase in the supply of TEAs will change that balance. It was expected that the supply of TEAs within the peat would be detrimentally affected by the addition of biochar. However, this study found that applying biochar to the surface of a peatland enhanced carbon storage whilst not affecting the supply of TEAs within the peat soil water.

3.4.5.1. Iron

Though Treatment was not significant in detrimentally changing the concentration of iron in the soil water, iron concentrations at Hatfield are high, relative to concentrations observed at many peatland sites regardless of Treatment and management. Worrall and Adamson. (2008) found no significant change in the median concentration of iron in peat water after burning (with concentrations of approximately 0.35 mg Fe/l before and 0.38 mg Fe/l after burning). Similarly, Boothroyd et al. (2021) reported iron concentrations at Moor House of 0.17 and 0.21 mg Fe/l at 10 cm and 50 cm. The mean absolute iron concentration on Treatment plots at Hatfield was 2.1 ± 0.77 mg Fe/l. The main way in which lowland raised bogs lose water is through evaporation, therefore high iron concentrations may be due to an evaporative effect. Labadz et al., (2007) demonstrated that during warmer months when water table decreased there was increased concentrations of certain elements, iron being one meaning relatively high iron concentrations of iron at Hatfield could be explained by an evaporative effect. However, when plotting iron concentration against conductivity (Figure. 3.14) it shows that high iron concentrations and high conductivity act independently of one another meaning that an evaporative effect may not be the only explanation. If an evaporative effect took place, a stronger relationship between iron concentration and conductivity would be expected an evaporative effect would have a similar effect on both factors.

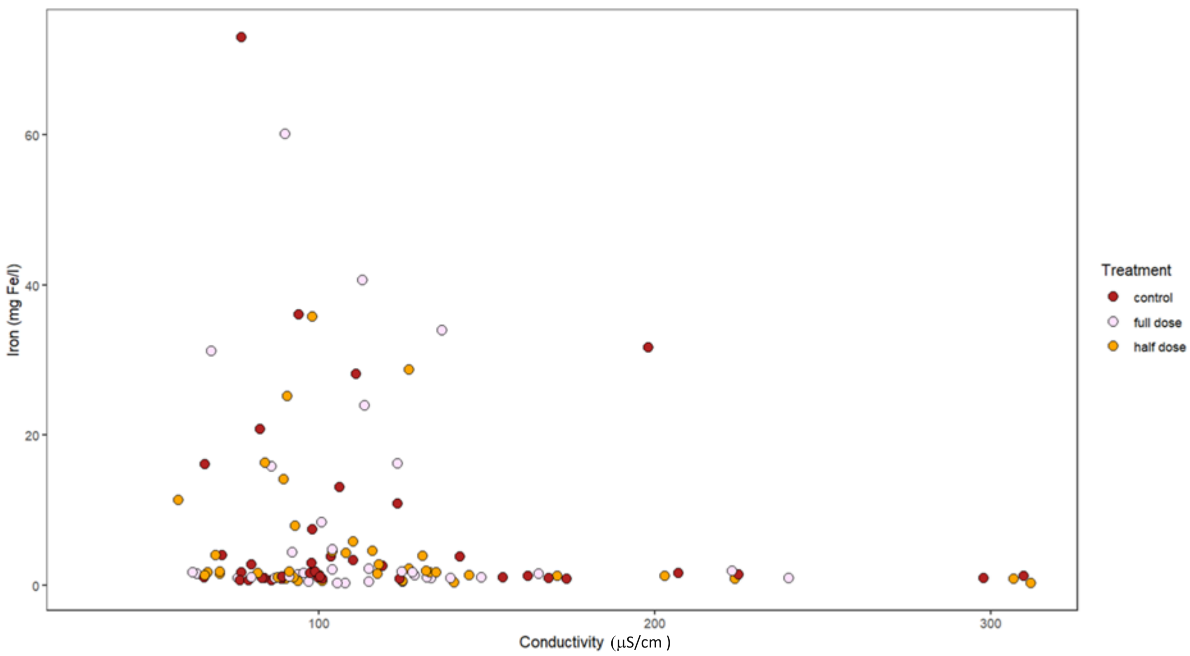

Figure 3.14. Plot of relative iron soil water concentration against conductivity of peat soil water.

3.4.5.2. Sulphate

Sulphate concentration was not significantly different after the application of biochar with and without covariates, nor over time. Mean absolute sulphate concentration at Hatfield on half- and full-dose Treatment plots was 1.70 ± 0.37 mg S/l compared to the pre-treatment control concentrations.

A study by Novak et al. (2005) reported sulphate concentrations at Thorne Moors of 4.9 ± 0.4 mg SO^{2-}_4 mg/l^{-1}. Mean absolute sulphate concentrations at Hatfield on half- and full-dose Treatment plots was 1.70 ± 0.37 mg S/l. At Moor House mean sulphate concentration was 0.11 mg S/l at a 10 cm depth and 0.02 mg S/l at 2 cm. The absolute concentrations in my study are thus greater than that at Moor House but less than that at Thorne Moors. It would be expected that the concentrations would be somewhat similar in Thorne and Hatfield Moors due to their proximity.

A prescribed burn management study by Worrall and Adamson (2008) found that prior to burning the median concentration of sulphate in the soil water was 0.3 SO_4 mg/l, and there was no significant change in sulphate concentration after burning. Compared to, my study observed median sulphate concentration of 1.02 mg S/l is higher than those found by Worrall and Adamson (2008). The presence of a higher concentration of sulphate than observed in other management studies, means that there could be no change in the CH_4 flux because sulphur is reduced fully before CH_4 is emitted. Hence the presence of sulphur means it has not been fully reduced and therefore no CH_4 was being released from the soil.

3.5 Water quality conclusions

- Treatment with biochar significantly increased the conductivity. Mean conductivity without biochar treatment was 105.65 with the addition of a full dose of biochar the conductivity was 109.79. The addition of biochar had 2% significance of the conductivity of the pore water. The significance of biochar treatment on increased conductivity diminished with time.
- Treatment with biochar significantly increased the absorbance. Mean absorbance without biochar treatment was 0.44 Au with the addition of a full dose of biochar the absorbance was 0.57 Au. The addition of biochar had 2% significance of the absorbance of the pore water. The significance of biochar treatment on increased absorbance persisted with time.
- Treatment with biochar significantly increased the nitrate. Mean nitrate without biochar treatment was 0.02 mg N/l with the addition of a full dose of biochar the nitrate concentration was 0.03 mg N/l. The addition of biochar had 2% significance of the nitrate concentration of the pore water. The significance of biochar treatment on increased nitrate concentration diminished with time.
- There was no change in the TEA supply within the peat soil water with the application of biochar meaning biochar did not cause an influx of fresh TEAs.
- When differences in water table were considered pH, DOC and phosphate significantly increased, meaning water table was masking the effect of biochar treatment, which persisted with time.
- The raised bog environment showed that evaporative concentration played an important role in controlling the water table.

4. The effect of biochar on CO_2 gas fluxes of a lowland raised bog

4.1 Introduction

This chapter continued the work on evaluating the application of biochar to peatlands to enhance carbon sequestration: in this chapter examining the effect of biochar on vegetation growth and gas flux parameters.

Peatlands are classified as a carbon sink when the rate of primary productivity exceeds decay, as outlined in chapter 1. Over many years vast amounts of CO_2 have been stored in peatlands. However, due to increasing anthropogenic climate change, peatlands need to be improved as a carbon sink. Applying biochar onto the surface of the peatlands has the capacity to increase the carbon store within peatlands, however, biochar has not been applied to peatlands before. In consequence, this chapter studies the effect that applying biochar on to the surface of the peat had on the growth of native vegetation. Additionally, this chapter considers the gas fluxes of peatlands and whether applying biochar onto the surface will stimulate the release of CO_2.

4.2 Gas flux field methods

4.2.1 NER, NEE, and GPP

Measurements of CO_2 gas fluxes between land surface and the atmosphere were carried out using a portable infrared gas analyser (IRGA) (EGM-5, PP systems, Hitchens, UK) with a transparent CPY chamber. The gas chamber is cylindrical in shape, which allowed for better mixing of enclosed air than other chamber shapes and was constructed from non-permeable materials (Pavelka et al., 2018). The transparent PVC chamber was placed over the gas collars located within each of the 27 treatment plots. Soil gas collars serve as an airtight seal between the chamber and the peatland surface. These collars were made from non-reactive materials and were carefully put into the ground in February 2022 as to limit disturbance of the vegetation, soil and roots within the peatland (Pavelka et al., 2018). Gas collars were left for two weeks prior to the first set of gas measurements to avoid measuring small disturbances caused by installing gas collars (Li et al., 2021).

Measurements of CO_2 flux were taken for two minutes at each plot, and the chamber was flushed with air for twenty five seconds between measurements to calibrate the equilibrium between atmospheric air and air in the chamber headspace (Xu et al., 2005). Measurements were taken during daylight hours. Two CO_2 flux measurements were made at each collar on each visit. The first measurement was of net ecosystem exchange (NEE), i.e., the difference between gross primary productivity (GPP, the absorption of CO_2 via photosynthesis) and ecosystem respiration (ER, the release of CO_2 into the atmosphere, Dyukarev, 2017). The second measurement was of ER which was measured in dark conditions by covering the chamber with an opaque cover to prevent photosynthesis. The difference between the NEE and ER measurement corresponds to the GPP value. During each measurement, CO_2 concentrations (ppm) were recorded every ten seconds. After every three NEE readings, photosynthetic active radiation (PAR) and air temperature were recorded.

4.2.2 Albedo

Albedo (α) is defined as the ratio of incoming surface radiation and reflecting solar irradiation, perpendicular to the Earth's surface (Matthias et al., 1999). Albedo was measured in this trial to distinguish between bare soil and vegetation. Albedo of each of the 27 treatment plots was measured using a handheld pyranometer with a separate sensor (MP100, Apogee Instruments, Logan, UT) in the same marked corner of each plot. Five albedo readings were taken at each plot once a month between February 2022 and May 2023. The pyranometer was held over the surface of each plot at around half a meter from the surface of the peatland (Sailor et al., 2006). Albedo was then measured by firstly holding the pyranometer sensor face up, recording incoming solar radiation, after which the pyranometer was inverted to read the outgoing radiation. Each time the pyranometer was turned it was held for five seconds to reach equilibrium before a new measurements was taken (Sailor et al., 2006): the albedo is the ratio of these two measurements and as such values range from 0 to 1. The handler of the pyranometer stood so as not to cast a shadow over the plot.

4.2.3 Fixed position photographs

Fixed position photographs and albedo data were taken at the same marked corner of each plot each month, using a quadrat. To access this corner of the plot, which in most, but not all cases was at the furthest corner from where other sampling was carried out within the box plot.

The red, green, blue (RGB) colour model was used in this study to monitor the growth and any changes in vegetation growth after biochar addition. Measures used in RGB were the contrasts of relative red (Rgg), green (Ggg), and blue (Bgg) data. In this study red data were extracted at first followed by green due to the order of colour absorption during photosynthesis.

4.3 Statistical analysis of gas flux

4.3.1 Analysis of variance (ANOVA) and Covariance (ANCOVA)

The experimental design and subsequent analysis follow the pattern outlined in section 3.3.1. ANOVA was used to analyse Treatment as a factor and the Month*Treatment interaction in order to assess the application of differing levels of biochar treatment applied on the surface of a peatland. The ANOVA was used to assess NEE, NER, GPP, albedo and RGB. For NEE, NER, GPP, albedo, Rgg, and Ggg photosynthetic active radiation (PAR) and air temperature (Ta) were included as covariates. In which cases the analysis was performed first without, and then with the inclusion to test the importance of the covariate in explaining, or not, the impact of that covariate on each of NEE, NER, GPP, albedo, Rgg, and Ggg.

Both relative and absolute data were used during ANOVA and ANCOVA analysis. Relative data were used to demonstrate change relative to control plots. As there were no pre-treatment gas flux data, data are relative to the control plots for each month of the study. Absolute data were used to provide contextual application to wider literature.

4.3. CO_2 gas flux results: NEE, NER, GPP, RGB, Albedo

Table 4.1. Summary of results for this chapter - arithmetic mean and range. Positive values of gas fluxes are fluxes to the atmosphere.

Determinand	No. data points	Full dose mean	Half dose mean	Control dose mean	Overall mean	Full dose range	Half dose range	Control dose range	Overall range
Absolute NEE (mg CO_2/cm^2/day)	484	0.09	0.1	0.07	0.08	-0.17 - 0.83	-0.06 - 0.84	-0.33 - 0.86	-0.33-0.84
Absolute NER (mg CO_2/cm^2/day)	480	0.09	0.08	0.09	0.08	-0.01 - 0.67	0.007 - 0.84	-0.02 - 0.62	0.007 - 0.84
Absolute GPP	484	-0.001	-0.002	-0.001	-0.001	-0.019 – 0.038	-0.034 - 0.025	-0.019 - 0.023	-0.034 – 0.038
Relative albedo	2265	0.17	0.18	0.18	0.18	0.04 - 0.37	0.07 - 0.40	0.02 – 0.45	0.02 - 0.45
Absolute Rgg	407	0.35	0.34	0.34	0.34	0.31 - 0.41	0.30 - 0.43	0.30 - 0.41	0.30 - 0.43
Absolute Ggg	407	0.29	0.28	0.25	0.27	0.22 - 0.39	0.20 – 0.36	0.20 - 0.38	0.20 - 0.39

Table 4.2. Summary of ANOVA results - percentage importance of original variance of determinants. ***Significant factor or interaction at $p < 0.05$.**

Determinant	Month	Cell	Location	Treatment	Month*Treatment	Month*Location	Month*Cell	Treatment*Location	Treatment*Cell	Location*Cell	R^2
NEE	**8***	0	1	**5***	10	5	8	**4***	1	1	0.549
NER	**13***	8	5	2	26	25	**27***	4	10	8	0.536
GPP	**13***	9	5	2	26	25	28	4	10	9	0.270
Albedo	**15***	**2***	**2***	**2***	**30***	**30***	**29***	**4***	**4***	**4***	0.455
Rgg	15	2	**2***	**2***	30	30	27	4	4	**4***	0.376
Ggg	15	2	**2***	2	30	30	27	4	4	**4***	0.301

Table 4.3. Summary of ANCOVA results – percentage of original variance explained of the determinants with water table, air temperate (Ta) and photosynthetic active radiation (PAR) as a covariates. ***Significant factor or interaction at p > 0.05.**

Determinant	Relwt	Ta	PAR	Month	Cell	Location	Treatment	Month*Treatment	Month*Location	Month*Cell	Treatment*Location	Treatment*Cell	Location*Cell	R^2
NEE	1	1	1	**13***	**4***	**3***	**2***	26	21	**26***	**5***	4	**4***	0.536
NER	1	1	1	**13***	**4***	5	2	**26***	**25**	**28***	4	**6***	7	0.524
GPP	1	1*	1*	**13***	4	5	2	26	25	29	**4***	**6***	6	0.266
Albedo	1	1	1	**15***	**2***	**2***	**2***	**30***	**30***	**29***	**4***	**4***	**4***	0.470
Rgg	**1***	1	1	**15***	**2***	**2***	**2***	**30***	**30***	27	**4***	**4***	**4***	0.665
Ggg	1	1	1	**14***	**2***	**2**	2	28	28	**25***	**4***	**4***	**4***	0.733

4.3. Gas flux and vegetation results

4.3.1. Net ecosystem exchange (NEE)

In total, 484 measurements were taken of NEE. Mean NEE across Treatments was positive (a flux into the atmosphere) at 0.08 mg CO_2/cm^2/day (Table 4.1). Prior to the statistical analysis, the Anderson Darling test was performed and data were found to be normally distributed. Absolute data were used for gas flux as it is necessary to show actual CO_2 released from biochar addition. The ANOVA of absolute NEE data showed Treatment was significant at $p < 0.05$ and explained 5% of the original variance (Table 4.2, Figure 4.1). With the inclusion of relative water table, photosynthetically active radiation (PAR) and air temperature (Ta) Treatment remained significant (Table 4.3) and none of these covariates were significant. The Month*Treatment interaction was insignificant ($p > 0.05$) with and without the inclusion of relative water table, PAR and Ta. The post hoc Tukey test suggests a significant difference between all combinations of Treatment levels.

The lack of a significant Month*Treatment interaction and no significant covariates means that the annual NEE budget can be simply scaled from the Treatment factor. Over the course of a year this implies that the annual NEE isa positive flux into the atmosphere of 328.5 ± 0.01 g CO_2/m^2/year for the full dose scenario, 365.0 ± 0.01 g CO_2/m^2/year in case of the half dose scenario, and 255.5± 0.01 g CO_2/m^2/year without biochar treatment. Hence biochar addition resulted in an additional NEE flux of 109.5 ± 0.01 g CO_2/m^2/year.

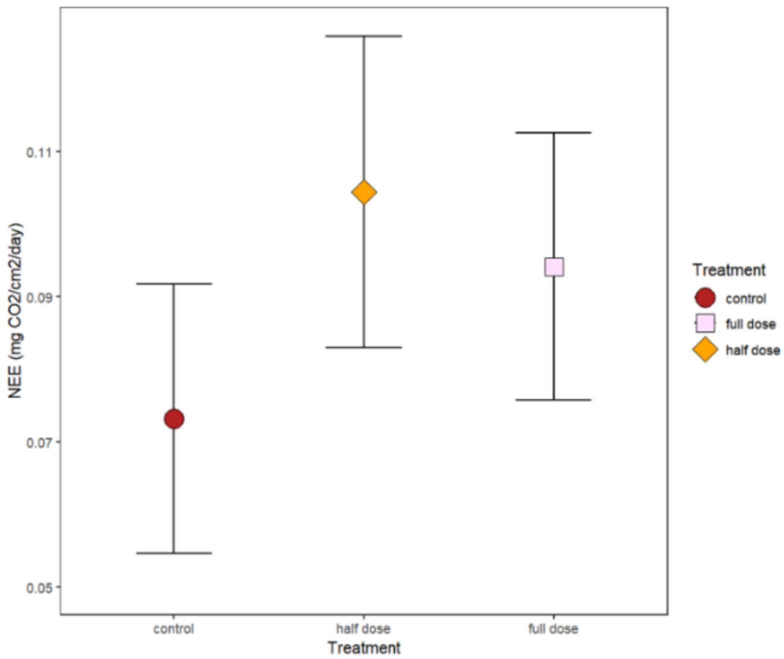

Figure 4.1. Main effects plot of Treatment of NEE compared to monthly levels. The datapoint is the marginal mean and the whiskers are the 95% confidence interval.

4.3.3 Net ecosystem respiration (NER)

There were 480 measurements of NER. Prior to analysis, the Anderson Darling test was performed and data were found to be normally distributed. The ANOVA of absolute NER data showed Treatment was not significant at $p < 0.05$, the Month*Treatment interaction was also not significant at $p < 0.05$ (Table 4.2). When the ANCOVA was performed including covariates of relative water table, PAR, and Ta, the Treatment and the Month*Treatment interaction remained insignificant as covariates were not significant (Table 4.3). The lack of a significant Treatment and Month*Treatment interaction means the there was no measurable difference between treated and control plots, as such the mean absolute NER flux across all Treatment levels was a positive flux into the atmosphere of 1.1 ± 0.01 gCO_2/m^2/day (Table 4.1). The NER peaked in the summer months but this effect was not explained by changes in the measured covariates. The lack of significant Treatment factor and Month*Treatment interaction means that NER from the site scales to a yearly positive flux into the atmosphere of 401.5 ± 0.01 g CO_2/m^2/year.

4.3.4 Gross primary productivity (GPP)

There were 484 GPP measurements, mean absolute GPP across all Treatment levels was -0.01 ± 0.0005 gCO_2/m^{-2}/day, i.e. a mean flux from the atmosphere to the land (Table 4.1). Over a year this would mean an intake of CO_2 averaged across all Treatment levels of 3.65 ± 0.18 gCO_2/m^{-2}/year from the atmosphere.

Prior to analysis, the Anderson Darling test was performed and data were found to be normally distributed. The ANOVA of absolute GPP data showed Treatment was not significant at $p < 0.05$. The Month*Treatment interaction was also not significant at $p < 0.05$. Treatment as a factor remained insignificant when ANCOVA with relative water table, PAR and Ta was performed. Within the ANCOVA, both PAR and Ta were significant at $p < 0.05$, each had a 1% effect size on the original variance, though their inclusion made no difference to the importance of the Treatment factor. Relative water table as a covariate was insignificant (Table 4.3).

The lack of a significant Treatment or Month*Treatment interaction means that the annual GPP budget can be scaled from the mean measurement. Over the course of a year, this equates to a mean CO_2 intake of 3.65 ± 0.18 gCO_2/m^{-2}/year. The absence of a significant Treatment effect means that biochar addition had no impact upon GPP, i.e. within the restriction of chamber measurements there was measurable GPP change, but no measurable impact of biochar on peatland flora.

4.3.2. Albedo

There were 2266 measurements of albedo, and the mean absolute albedo across Treatment levels was 0.18 ± 0.002 (Table 4.1). Prior to analysis, the Anderson Darling test was performed and data were found to be normally distributed. The ANOVA of absolute albedo showed Treatment was significant at $p < 0.05$, explaining 2% of the original variance (Table 4.2, Figure 4.2). The Month*Treatment interaction was significant at $p < 0.05$ and explained 30% of the original variance (Table 4.2) (Figure 4.3).

The mean difference between full dose and control albedo during the first month of sampling in February 2022, i.e. prior to biochar application, was 0.001. The mean difference between full dose and control albedo during the last month of sampling in May 2023 was -0.001. The largest difference in mean albedo between full dose and control plots was observed in June 2022 where the difference was 0.045. The smallest difference after biochar application between full dose and control plots was observed in May 2023 (Figure 4.4).

ANCOVA with the inclusion of water table, PAR and Ta as covariates, Treatment and the Month*Treatment interaction remained significant (Table 4.3). The post hoc Tukey tests showed a significant difference between all Treatment level combinations.

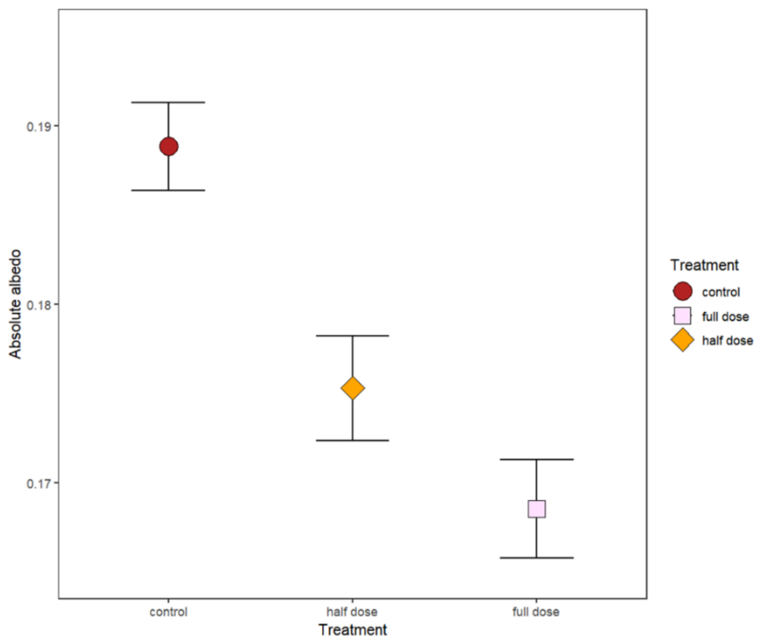

Figure 4.2. Main effects plot of Treatment of albedo relative to pre-treatment levels. The datapoint is the marginal means and the whiskers are the 95% confidence interval.

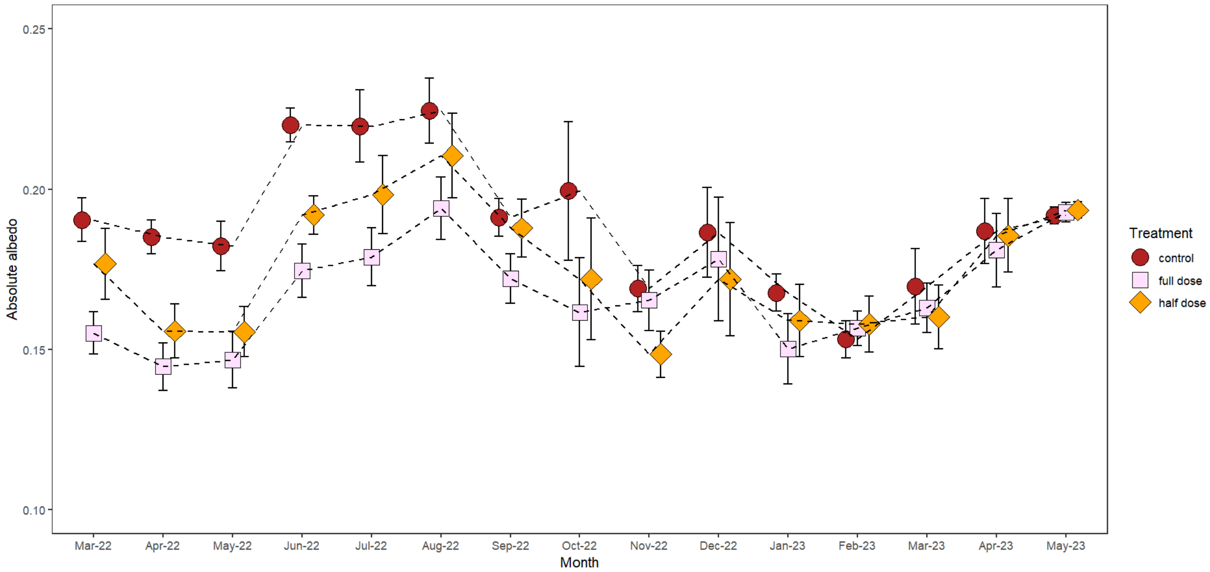

*Figure 4.3. Main effects plot of the Month*Treatment interaction of absolute albedo. The datapoint is the marginal means and the whiskers are the 95% confidence interval. The plotted points are offset around the Month factor levels to ensure visibility.*

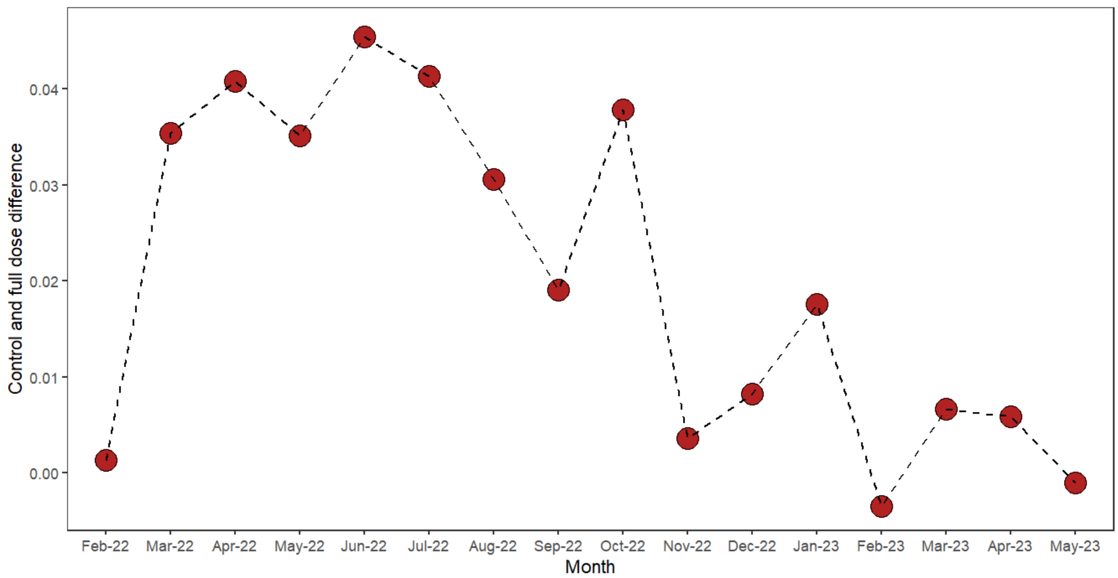

Figure 4.4. The difference between monthly mean albedo of control and monthly mean albedo full dose Treatment. February 2022 showing the pre-treatment month.

4.3.5 Fixed position photographs

There were 405 fixed position photographs. Prior to analysis, the Anderson Darling test was performed, and data were found to be normally distributed. The ANOVA of the absolute ratio of red pixels (Rgg) data showed that Treatment as a factor and the Month*Treatment interaction were not significant at $p < 0.05$ (Table 4.2). With the inclusion of water table, PAR and Ta as covariates, the Rgg Month*Treatment interaction became significant (Figure 4.5). Covariates explained 30% of the original variance, and relative water table was the only significant covariate at $p < 0.05$, having a 1% effect on the original variance (Table 4.3).

The ANOVA of the ratio of green pixels (Ggg) data showed Treatment was significant but not over time i.e. the Month*Treatment interaction was not significant at $p < 0.05$ (Table 4.2, Figure 4.6). When ANCOVA with relative water table, PAR and Ta was performed on Ggg data, Treatment and the Month*Treatment interaction remained insignificant due to the lack of significant covariates (Table 4.3). The post hoc Tukey test showed no significant difference between any combination of Treatment levels.

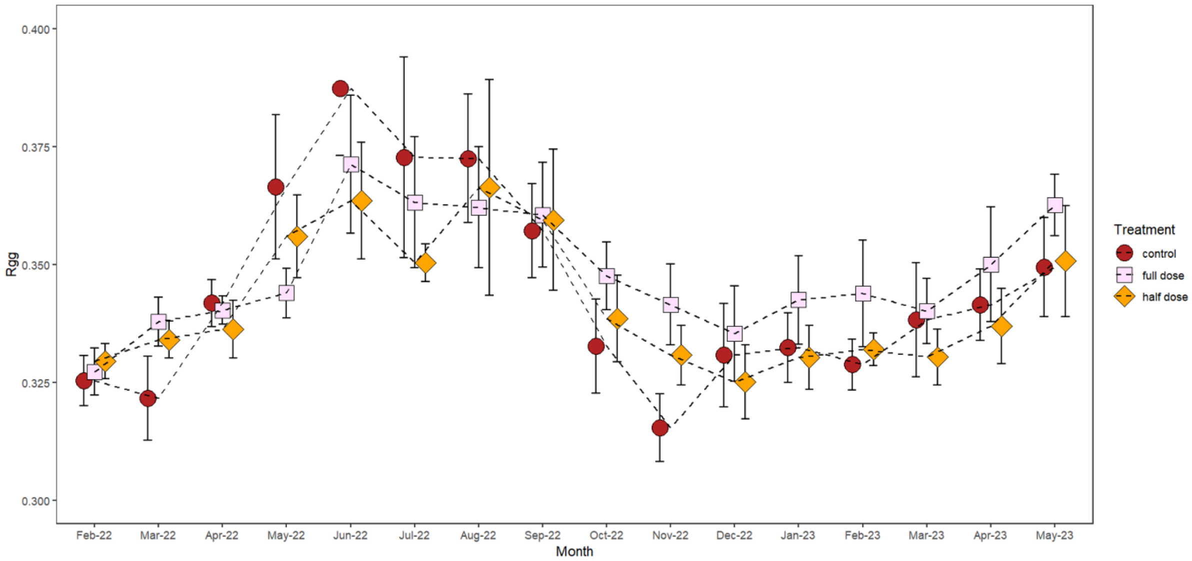

*Figure 4.5. Main effects plot of the Month*Treatment interaction of absolute Ggg. The datapoint is the marginal means and the whiskers are the 95% confidence interval. The plotted points are offset around the Month factor levels to ensure visibility.*

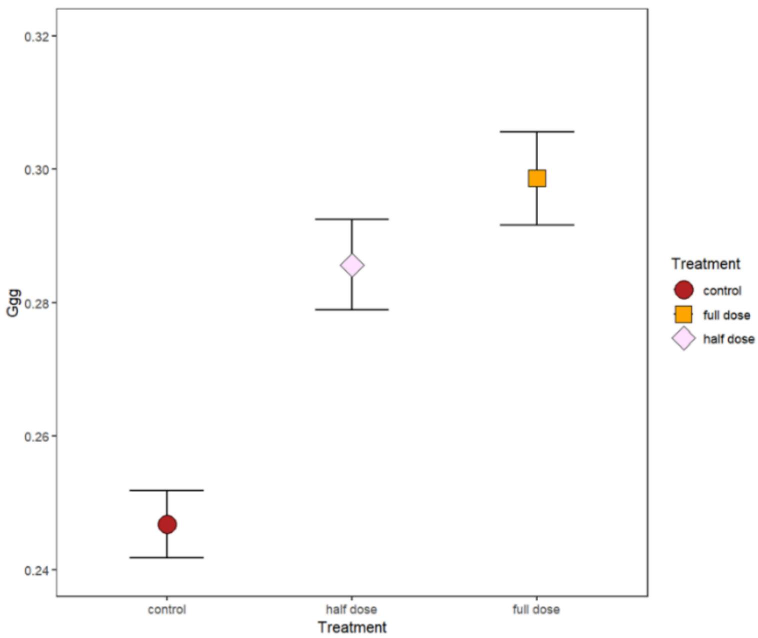

Figure 4.6. Main effects plot of Treatment of Ggg relative to pre-treatment levels. The datapoint is the marginal means and the whiskers are the 95% confidence interval.

Figure 4.7.a Tilney wet high 15/03/22 – Month of biochar addition.

Figure 4.7.b Tilney wet high 02/05/23 – End of sampling. 15 months after biochar addition.

Figure 4.7.c Tilney inter high 05/05/22 two months after biochar application cotton grass growth.

Figure 4.7.d Morland inter high 02/05/23 cotton grass growth at end of sampling.

Figure 4.7.e Thorpe dry high 15/03/22. Month of biochar addition.

Figure 4.7.f Thorpe dry high 02/05/23 15 months after biochar addition end of sampling.

4.4. Gas flux and vegetation discussion

Biochar was applied to the surface of a peatland to enhance the carbon storage of a former lowland raised bog. This study assessed the effect of biochar application on the exchange of CO_2 from peat soils, assessing whether C storage was enhanced, or whether CO_2 fluxes were detrimentally changed. Any additional CO_2 release could have been from the peat or from the biochar. To understand the impact of the biochar, the vegetated surface was then monitored by measuring albedo and using fixed position photography.

The study found a significant difference between treatments for NEE but not for either NER or GPP. Furthermore, there was no trend over time in any of the treatment effects. This implies that biochar had only a limited effect on CO_2 exchange on this peat soil. The lack of significant effect for GPP implies no measurable impact upon the vegetation of the treated plots. Monitoring using the albedo showed a significant effect of biochar, however, the impact diminished with time as the vegetation re-emerged in May 2023 - 15 month after biochar was first applied. Additionally, fixed position photography showed no significant difference between Ggg pixel ratio of treatment and control plots; Rgg was only significant when water table depth was considered meaning differences in water table depth were masking the effect of the biochar.

Previous studies assessed the effects of managed burning on gas fluxes. Clay et al. (2015) observed a significant increase in NEE after burning, reporting fluxes equivalent to -31.44 to 14.4 $gCO_2/m^2/day$. In my study at Hatfield, mean absolute NEE fluxes of Treated plots were 0.8 $gCO_2/m^2/day$, therefore within the range of observed on peatlands with managed burning. Though biochar had not been applied to peatlands before it has been applied to soils. Yang et al. (2019) found biochar application to improve soil as a C sink, sequestering the equivalent of 27.90 to 39.21 $gCO_2/m^2/day$ when 40 tons/ha of biochar were applied. Conversely, I found that the biochar application at Hatfield significantly increased the positive NEE flux into the atmosphere of 0.8 $gCO_2/m^2/day$. Azeem et al. (2019) also found that the application of biochar disturbed the soil and increased the carbon flux into the atmosphere, observing a flux equivalent to 1,296 and 1,824 $gCO_2/m^2/day$ depending on the C content of biochar applied. This observed flux is substantially higher than the flux observed at Hatfield, where biochar application resulted in mean positive fluxes of 0.8 $gCO_2/m^2/day$.

There was no significant effect of biochar application on NER fluxes at Hatfield, suggesting that biochar had no measurable effect on vegetation growth and respiration. As biochar had no significant effect on NER fluxes it would be expected the NER would be similar to that of a fully vegetated peatland. Worrall et al. (2011) found that vegetated, unburnt peatland had a positive atmospheric NER flux equivalent to 0.43 $gCO_2/cm^2/yr$. This observed flux is greater than that emitted on across all Treatment levels at Hatfield where the NER flux was 0.04 $gCO^2/cm^2/yr$.

With respect to albedo, no studies could be found that considered the impact of management upon albedo. Petzold and Renez (1975) give albedo values for a range of surfaces in a Canadian sub-Arctic peatland environment and reported values range from 0.07 (s.d. 0.006) for bare surface and 0.26 (s.d.0.2) for a dry lichen surface – there was no *Calluna vulgaris* or *Eriophorum spp.* in their study. Miranda (1982) did measure albedo for *Calluna vulgaris* and measured average albedo for dry canopy of 0.11 (95 % confidence interval (C.I.) 0.09 - 0.13), and for wet canopy of 0.18 (95 % C.I. = 0.15 - 0.21). Worrall et al. (2020) measured values of albedo for Thorne Moors and found mean values of: arable =0.22 (95% C.I. = 0.11–0.54); vegetated peat = 0.19 (95% C.I.= 0.08–0.38); dry bare peat = 0.08 (95% C.I. = 0.05–0.14); and snow = 0.68 (95% C.I. = 0.51–0.83). Therefore, the mean albedo of Treatment plots of 0.18 ± 0.002 measured in this study are within the range reported of a vegetated peatland. Additionally, there was no observed difference in GPP between control and Treatment plots at Hatfield. Implying that biochar did not detrimentally affect the growth of vegetation, but also did not enhance the growth of vegetation to any measurable extent.

The impact of biochar on vegetation growth was assessed with fixed position photographs. There was a significant increase in the ratio of Ggg pixels with biochar Treatment, meaning there was a statistically measurable change in vegetation cover after biochar application. However, this difference diminished with time. As would be expected, immediately after biochar addition (Figure 4.8 and figure 4.12) biochar dominated the surface of the bog. However, as the statistical change in Ggg pixels diminished with time, the regrowth of vegetation through the biochar increased with time. Figure 4.9. and figure 4.13. both show native cotton grass and sphagnum moss growth 15 months after biochar addition showing biochar only had an initial effect on vegetation growth.

The ratio of Rgg pixels with and without Treatment was only significant over time when water table as a covariate was included. Rgg likely only became significant due to the high water table levels meaning surface water often covered the plots meaning when photographs were taken and the pixel data extracted the dark coloured water would dominate the pixel ratio, rather than the biochar or vegetation.

Closed chamber studies can limit the development of plants, and the actual size of the gas chamber used could limit the development of vegetation, and therefore the measurement of CO_2 flux (Morton and Heinemeyer. 2018). However, the same closed chamber system was used for each Treatment and so any effect would have occurred for every Treatment and control plot. Equally, it would have been expected that any limitation of the insertion of the gas collars would diminish with time over the course of the study which should have resulted in a significant Month*Treatment interaction. The lack of this interaction indicates that the insertion of the collar did not impact the measurements. Furthermore, the albedo measurements suggests that vegetation rapidly recovered from a 2 cm depth of biochar application and so we could expect it to recover from gas collar insertion within the experiment.

The study could not sample evenly across the year. There were no means of sampling when the water tables were sufficiently high that water was in the collars, this meant that during the winter through to early spring the number of measurements declined (Table 4.4).

However, the design of the experiment means that the treatment and control plots were in a factorial design with the Location factor, i.e. there were always plots that were high relative to the water table frame on the study site, thus not submerged and so could be used for flux measurements.

The result of the analysis means that simple estimates of the impact of biochar on greenhouse gas fluxes and C storage can be made. The statistical significance of the Treatment factor, but lack of Month*Treatment interaction for NEE means that the Treatment main effects can be simply rescaled as means of estimating annual budgets. This study assessed a peatland for a period of only 15 months, it is therefore not possible to understand the nature of the biochar decomposition kinetics. However, if zero-order kinetics are assumed, i.e. assuming the rate of biochar loss is the same every year, then the residence time can be estimated. The results of rescaling show that applying a full dose of biochar results in a positive flux into the atmosphere of 328.5 g $CO_2/m^2/yr$. This accounts for 0.4% of the applied biochar in a full dose per year resulting in an overall residence time of 240 years (Table 4.5). A half dose of biochar resulted in a yearly flux of 365 g $CO_2/m^2/yr$, meaning biochar is lost at a rate of 0.6% per year, therefore, having an overall residence time of 160 years (Table 4.5). It is hence reasonable to assume that less than 1% of the added carbon is returned to the atmosphere in a year.

Table 4.4. number of gas flux readings able to be taken during each month of the study.

Month	**Number of gas flux readings**
April 2022	12
May 2022	19
June 2022	18
July 2022	23
August 2022	27
September 2022	27
October 2022	27

November 2022	27
December 2022	16
January 2023	20
February 2023	18
March 2023	14
April 2023	17
May 2023	17

Table 4.5. Gas flux, biochar lost, and biochar residence time given NEE measurements with the assumption of zero-order kinetics. NEE flux, percentage of biochar lost were taken at 95% confidence.

Treatment	NEE flux (g CO_2/m2/yr)	% of biochar lost/yr	Biochar residence (yrs)
Full dose	328.5	0.4	240
Half dose	365	0.6	160
Control	255.5		

4.5. Gas flux and vegetation conclusions

- Treatment with biochar significantly increased the net ecosystem exchange (NEE) flux independently of the Month factor the positive NEE flux into the atmosphere persisted but did not change over time i.e., NEE remained a positive flux into the atmosphere but did not increase or decrease.
- Even though NEE increased, this was small relative to the additional C stored and it would take 240 for equivalent C stored within biochar to be emitted if NEE fluxes continued at the same rate.
- Treatment with biochar made no significant difference to the net ecosystem respiration (NER) flux. i.e. Hatfield remained a positive C flux into the atmosphere even though this did not diminish over time it also did not worsen with the addition of biochar.
- Treatment with biochar made no significant difference to gross primary productivity (GPP).
- The addition of biochar Treatment resulted in a significant decrease in albedo, though this effect diminished over time.
- Treatment with biochar significantly increased the Rgg ratio, which did not diminish with time. Increased Rgg pixels can be attributed to water on the surface of the plots rather than a detrimental change in vegetation growth.
- When water table, photosynthetic active radiation (PAR) and air temperature (Ta) were considered the pattern of significance did not change meaning covariates were not masking the effect of biochar treatment application vegetation growth and gas fluxes.
- Biochar application did not affect the growth of vegetation cover over 15 months.

5. Discussions and conclusions

Peatlands are large stores of C but slow sinks relative to the rate of anthropogenic climate change. For the potential of peatlands as a C store to be achieved and NetZero targets achieved, the C sink of peatlands needs to be enhanced. Though there are many well established peatland management practices, none aim to directly improve the C sequestration of peatlands over and above what its own natural rate of accumulation would be. This study has proposed that the application of biochar to the surface of a peatland directly enhances C sequestered and increases C stored in a long term C store.

The overall objectives of this study were to assess the effects of the application of biochar on water quality, gas flux and vegetation of a lowland raised bog.

5.1. Water quality

- Treatment with biochar significantly increased absorbance of peatland soil water regardless of the Month factor. i.e. Treatment had a persisting increase on absorbance that did not dimmish with time. The absorbance observed on treated plots was within that range of other peatland management practices., Additionally, the increase in absorbance, though significant was small relative to the control, so would not cause any detrimental effect to the peatland.
- Treatment with biochar significantly increased soil water conductivity and the concentration of nitrate, however this increase diminished over time.
- When relative water table was included as a covariate, Treatment with biochar significantly increased the concentration of DOC and pH. Meaning that differences in water table were masking the effect of biochar. DOC and pH increased independently of the Month factor, meaning biochar had a persisting effect over time. Even with a persisting increase in DOC and pH after biochar application were still within the range of near-natural and other managed peatlands, relatively, biochar did not cause a tangible difference to peatland function.
- Biochar Treatment significantly increased the supply of nutrients onto the peatland over time the supply of nutrients increased, but did not significantly change the supply of terminal electron acceptors.
- The raised bog environment showed that evaporative concentration played an important role in controlling water table.
- Though biochar caused significant changes in some water quality parameters, these changes were within the range of other peatland management studies. The magnitude of tangible change to water quality caused by biochar is small.

5.2. Gas flux and vegetation

- Treatment with biochar significantly increased the NEE flux independently of the Month factor the positive NEE flux into the atmosphere persisted but did not change over time i.e., NEE remained a positive flux into the atmosphere but did not increase or decrease. The increase in NEE flux was small increase relative to the C sequestered by applying biochar and NEE fluxes of Treated plots did not exceed those observed in other studies.
- Treatment with biochar made no significant difference to the NER flux. i.e. Hatfield remained a positive C flux into the atmosphere even though this did not dimmish over time it also did not worsen with the addition of biochar.
- Treatment with biochar made no significant difference to GPP. With the addition of biochar, Hatfield remained a C sink.
- With the addition of biochar Treatment there was a significant decrease in albedo, though this represented a significant diminishing effect over time returning to pre application levels.
- Treatment with biochar significantly increased the Ggg ratio, which did not dimmish with time. Though increased Ggg pixels can be attributed to water on the surface of the plots rather than a detrimental change in vegetation growth.
- When water table, PAR and Ta were considered the pattern of significance did not change meaning covariates were not masking the effect of biochar treatment application vegetation growth and gas fluxes.
- Biochar application did not affect the growth of vegetation cover over 15 months.

5.3. Implications

Peatlands accumulate and sequester C relatively slowly compared to the rate of anthropogenic climate change. However, applying biochar to the surface at a rate of either 32 tonnes/ha or 64 tonnes/ha is equivalent to 10 to 20 years of peat growth respectively. Assuming that application of 32 tonnes/ha equates to 1 cm of biochar on the surface and 64 tonnes/ha would be equivalent to 2 cm of biochar on the surface. Therefore application of biochar quickly enhances the C sequestered and stored within a peatland.

Biochar Treatment significantly increased the NEE flux into the atmosphere. However, it would take 240 years before the equivalent C of that stored in a full dose of biochar to be emitted as CO_2. Despite the statistical changes in some water quality and gas flux parameters, such differences were small. It is unlikely they would cause any difference to the overall function of the peatland.

Peatlands are large stores of C. Adding biochar to the surface enhances the C sequestration and long term C storage. As there was no detrimental impacts to the vegetation growth, within the limits of this study's sampling, it can be suggested that biochar application would be applicable on other peatlands without negatively affecting the vegetation growth.

5.4. Study limitations

As for the water quality studies, regular inaccessibility to 3 plots from December 2022 until May 2023, as well as sporadic flooding of other gas collars during the study meant that gas flux readings could not be taken in full. However, this study was based on a factorial design meaning there were two other wet Locations where data were collected, meaning the cross classified nature of the data set were not compromised.

Additionally, it was only possible for 5 water samples to be collected during August and 13 in September due to the water table being too low for samples to be obtained. The volume of the sample collected during August and September was in some instances too small for all types of analysis, meaning there was depleted samples sizes for both months across all determinants. For nutrient and TEA analysis, each month only 9 out of 27 samples (where possible) were analysed for cost purposes. However, this was not an issues as the samples chosen for analysis were triplicated, meaning that for each month of sampling, all Cells, Locations and Treatment factors were analysed.

For all water quality determinants there were only one month of pre-treatment data available as opposed to a full year meaning that there was only one month of pre-treatment sampling available. However, there were 3 controls plots within each Cell, so a total of 9 control plots in addition to the one month of pre-treatment data. There was no pre-treatment gas flux data meaning each month of data were compared to the corresponding control that month, based on the Location factor. However, as the control plots were not hydrologically connected to treated plots, having no pre-treatment data was not a problem.

The size of the gas chamber used within this study was relatively small, so may not be representative of true GPP, however, the calculated GPP did account for the size of the chamber.

5.6. Future work

As this was the first time biochar has been applied to a peatland the effects on water quality and gas flux were not previously known. Although significant, the difference biochar treatment made to gaseous exchange of CO_2 was small relative to the amount of C sequestered and stored. There was also no detrimental impact of biochar addition on the vegetation growth: the native peat forming species were still growing 15 months after the biochar had been applied. As these were the case, biochar could be reapplied on top of the biochar applied 15 months previous. The main aim of this study was to enhance the C storage of the peatland, by reapplying biochar this would double the C stored on the peatland. It would be important to monitor the effect of reapplication, particularly on the growth of native vegetation. Reapplying biochar to the surface of the peatland could be repeated every few years to achieve an optimal C storage without compromising on the vegetation growth, water quality and gas flux. The reapplication of biochar has been applied before to mineral soil environment with 5 years of consecutive application, as there has been little tangible difference applying biochar to Hatfield this approach could be trialled (Lu et al., 2014).

As the significant effect biochar had on water quality and gas flux was small and in all cases except conductivity, diminished over time an additional trial could assess the effect of a higher dose of biochar being applied in one go rather than over time. As 32000 and 64000 kg/hectare were applied initially an increase of the same factor, so a dose of 96000 kg/hectare could be trailed applying a larger dose of biochar at once would mean more C was sequestered and stored at once.

There were several parameters that were not assessed in this study. For example, Methane (CH_4). CH_4 is a more powerful greenhouse gas than CO_2. As Treatment with biochar has some statistical increase in the CO_2 release into the atmosphere, measuring CH_4 release to see if biochar has disrupted the peat and stimulated the release of methane. Though this would be necessary to measure if biochar were to be applied on a large scale, as there was no change in the TEA concentrations then it is unlikely that methane release would be increased. However, this study only accounted for water from 27 dipwells so this is only representative of small pockets of the peatland and there may be areas, if the study was extended across a bigger area of Hatfield where TEA concentrations may differ. Therefore measuring methane alongside TEA analysis would be beneficial.

This study assessed only the vegetation cover on the peatland rather than the species type. As it is not just vegetation cover but vegetation species that is important for peat formation future work would need to be carried out to monitor whether Treatment with biochar was significantly change the species of vegetation growing. Similarly, the fauna species were not recorded or monitored during this study. Birds such as nightjars which are relatively rare, as such it would be important to monitor the numbers of such species after biochar application to ensure habitats were not being detrimentally affected.

To purchase 1 tonne of biochar it costs in order of £1,500. Therefore, the cost of applying a full of biochar across Hatfield which is 13.6 km^2, would be £130,560,000 and £65,280,000 if a half dose was applied. The price and availability of biochar on this scale would not be viable because there would not be enough organic biomass to produce this amount of biochar. An alternative to biochar such as biomass chips should be considered. Heather for example, is a native, but non peat forming species that could be removed and added to the peatland as heather brash. The addition of heather brash would be an effective infilling technique for the 5 m of extracted peat at Hatfield. However, the C content would not be as high as biochar and the residence time would likely not be as long, but the cost would be lower, so therefore the brash could be spread over a larger area more frequently, possibly storing the same amount of C .

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Appendix

Table 1. Chemical composition Hatfield Moors peat at depths 1 to 92.5 cm. Value quoted refers to the mean percentage of chemical composition of each depth. Values in brackets refer to the range within each depth of peat.

Depth (cm)	Carbon (%)	Hydrogen (%)	Nitrogen (%)	Oxygen (%)
1	48.64 (48.4-48.9)	5.10 (5.0-5.2)	0.65 (0.6-0.7)	33.03 (31.9-33.9)
3	48.54 (48.3-48.7)	5.04 (5.0-5.2)	0.69 (0.6-0.7)	33.24 (33.1-33.5)
5	49.24 (49.1-49.2)	5.13 (5.1-5.2)	0.71 (0.7-0.7)	32.77 (32.4-33.2)
7	48.17 (46.1-49.3)	5.14 (4.9-5.3)	0.64 (0.6-0.7)	33.26 (32.8-34.0)
9	48.05 (47.5-48.4)	5.13 (5.1-5.8)	0.56 (0.6-0.6)	33.30 (33.1-33.4)
11	47.81 (47.5-48.1)	5.20 (5.1-5.3)	0.53 (0.5-0.6)	34.02 (33.6-34.3)
13	48.06 (48.0-48.2)	5.16 (5.1-5.2)	0.61 (0.6-0.6)	32.90 (32.2-33.4)
15	48.24 (48.0-48.6)	5.21 (5.2-5.3)	0.55 (0.5-0.6)	33.37 (32.9-33.8)
17	48.07 (46.5-48.2)	5.32 (5.3-5.4)	0.71 (0.7-0.7)	31.12 (29.8-32.3)
19	47.40 (46.5-48.2)	5.26 (5.2-5.4)	0.65 (0.6-0.7)	31.11 (26.3-36.3)
22.5	48.44 (47.9-49.2)	5.15 (5.1-5.3)	0.63 (0.6-0.7)	32.84 (31.9-33.4)
27.5	48.92 (48.8-49.0)	5.37 (5.3-5.5)	0.61 (0.6-0.6)	33.77 (33.1-34.2)
32.5	49.69 (49.5-50.0)	5.41 (5.4-5.5)	0.72 (0.7-0.7)	32.59 (32.1-33.1)
37.5	46.88 (46.4-47.5)	5.15 (5.1-5.2)	0.52 (0.5-0.5)	34.23 (33.2-34.9)
42.5	50.71 (49.5-52.3)	5.73 (5.6-5.9)	0.76 (0.7-0.8)	33.52 (32.2-35.1)
47.5	49.55 (49.2-49.8)	5.36 (5.2-5.5)	0.79 (0.8-0.8)	32.22 (31.7-32.7)
55	50.46 (49.8-51.4)	5.40 (5.2-5.5)	0.79 (0.8-0.9)	32.17 (31.9-32.6)
65	49.37 (48.6-50.3)	5.22 (5.2-5.3)	0.67 (0.6-0.7)	32.56 (32.3-32.9)
75	50.18 (50.0-50.3)	5.23 (5.2-5.3)	0.58 (0.6-0.6)	33.05 (32.8-33.3)
85	47.84 (47.3-48.2)	5.35 (5.3-5.5)	0.87 (0.8-0.9)	33.77 (33.0-34.2)
92.5	47.70 (46.7-48.3)	5.16 (5.0-5.3)	0.86 (0.8-0.9)	33.09 (31.4-34.3)