Towards unravelling the peatland carbon cycle 'black box': Linking peatland management, habitat status, and climate to water chemistry and quality, and greenhouse gas fluxes

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February 2024

Abstract

UK blanket bog is a significant carbon (C) store and provider of ecosystem services, but historical mismanagement and recent climate change has led to destabilisation of soil C stocks and increased drinking water treatment costs in peatland draining catchments. To restore these services, a better understanding of the impacts of vegetation management, habitat restoration, and climate change upon peatland C cycling and water quality is required. Therefore, this thesis sought to assess the differences in C fluxes and water quality in blanket bog soils under different heather management regimes, habitat and restoration statuses, and climatic conditions.

Using a combination of field samples and a novel mesocosm experiment design, water quality and greenhouse gas fluxes were linked to heather management and peatland restoration practices and assessed alongside soil and climatic data. In-situ measurements from heather-managed blanket bog compared well with mesocosm measurements excluding methane flux. Vegetation management was beneficial for water quality but was accompanied by an increase in greenhouse gas emissions. Results indicated that the trajectory towards habitat recovery from degraded to an 'intact' status (i.e., functioning as a C sink) status following restoration is not straight-forward, given that there was a decline in water quality in mesocosms of recently restored habitats, likely attributed to disturbance following restoration. Water table depth decline and temperature increases associated with seasonal change led to increased dissolved organic C loading in porewaters but was accompanied by increased gaseous C uptake. Disinfectant by-products were produced following chlorination in all tested porewaters, and samples from cores dominated by vascular plants, especially Molinia had the lowest dissolved organic carbon removal rates. Therefore, it is suggested that managing heather-dominated blanket bog to maintain a desirable vegetation community composition (i.e., *Sphagnum* dominated) and higher water tables will increase blanket bog resilience and lower dissolved organic C concentrations. However, as higher methane emissions were associated with wetter sites, methane flux should be carefully considered as part of rewetting strategies.

This was the first study to directly assess C gaseous flux and water quality measurements from a field experiment comparing unmanaged, burnt, and cut heather-dominated blanket bog areas to paired peat mesocosms. It showed that, using a before-after-control-intervention approach, meaningful comparisons could be made between mesocosm and field measurements. Longer-term monitoring is recommended to enable better assessment of ecosystem service delivery trajectories, to help inform appropriate management and restoration practices aimed at protecting blanket bog ecosystem service provisioning in the context of unprecedented anthropogenic environmental change.

This thesis is written in loving memory of my Grandad Dixon who should be here to hold this thesis.

My PhD is dedicated to my sister, (Dr) Coral Mycroft, whom without, this thesis would not have been completed. I could never say thank you enough for your patience, love, and friendship.

Acknowledgements

This thesis is a culmination of the hard work and endless support of many people to whom I am very grateful.

I must first start by saying thank you to my supervisors, Andreas Heinemeyer and Kirsty Penkman. My PhD journey was tortuous at times, and their support and encouragement kept me going when it would have been much easier to give up. Additional thanks to Tim Thom and Jenny Banks as project partners who provided invaluable feedback and guidance throughout the course of the project.

There is a long list of people who have shared their time and knowledge to help me carry out this project. Deborah Sharp, Rebecca Sutton, Matt Pickering, and Mike Beckwith, Sam Presslee, and Scott Hicks who gave their field and laboratory expertise. Steve Cinderby, and Robert Mills as part of the thesis advisory panels whose comments improved my work and practices, and those working within the Biology workshop and University of York Estates who helped during the mesocosm and field site design and installation process.

The wider York Peat Team deserve a huge amount of credit for all the help with core collection, field, and laboratory work. Anthony Jones, Tom Holmes, Will Burn, and Bing Liu – I am very grateful for your friendship. Additional thanks are owed to (Dr) Will Burn who prior to me starting my PhD liaised with site owners to establish mesocosm core collection sites, field site acquisition and mesocosm design. Your groundwork meant the project got off to a great start.

Thank you to all of those working within SEI-York. You made the office a supportive and creative place to work with endless opportunities for tea and coffee breaks and knitting chats. Special thanks to Sarah West and Trudy Stapley who were nothing but kind and supportive during periods of great difficulty. SEI-York is very lucky to have you.

Thank you to the other PhD students with the E&G department. A special thank you to George Day for the endless board game evenings, coffee and cake trips, and encouragement when it felt like this thesis would never be finished.

To the Geography team at YSJ, thank you for your support and guidance. Special thanks go to Pauline Couper, Ben Garlick, Jude Parks, Suzy Fitzpatrick, Asmau Ahmed, Lucy Jones, and Toni Giblin.

Undertaking a PhD is difficult even without a global pandemic and the multiple health-related issues which have been thrown at me over the course of the project. The support from my mentor Sara Russel has been invaluable and I will always be grateful for her support. Thank you to QC Mary Prior and Judge

Gregory Dickinson QC for reminding me a point of great vulnerability, that this work was important. Thank you to Crohn's and Colitis UK for providing support following a life-altering diagnosis.

I would not be a scientist if it weren't for the support of my parents who have always encouraged me to be curious about and ask questions of the world around me. Thank you to the Stockdales and Reddyhoffs for being my northern family. Thank you, Rachael Adamson, and Claire Wilson-Bluss. I'll love you forever.

Finally, the biggest thank you to my partner, Jack. For all your patience, support, and the endless cups of tea. This thesis reflects your endless encouragement, especially during periods of great difficulty. I couldn't have done it without you.

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Declaration

I declare that this thesis is a presentation of original work, and I am the sole author. This work has not previously been presented for a degree or other qualification at this, or any other, University, or elsewhere. All sources are acknowledged as references.

Covid-19 mitigation statement

This project began in October 2018 and was planned to be finished at the end of September 2022. Due to exceptional circumstances (including Covid-19), I was given several extensions which led to this thesis being submitted in February 2024.

When the restrictions in lab access were put into place due to Covid-19, I was due to begin the work on drinking water treatment which would have meant approximately 12 months undertaking work in the laboratory on a full-time basis. Subsequently, this work began approximately 24 months later. This was partly due to restrictions on the development and use of new (to the department) methodology and a higher-than-normal demand on analytical instrumentation due to periods of restricted access. Prior to the pandemic, I had hoped to characterise the nature of organic matter within peat soils at a molecular level, with consideration for drinking water treatment, and link this to the implications of management, restoration, and climate. However, due to time limitations imposed by Covid-19 restrictions, this analysis was not undertaken. Whilst the main aims of the project have been achieved, there is still additional work to be done with some of the data collected which under ideal circumstances would have made it into this thesis. My hope is to complete this work post-viva.

Whilst not related to Covid-19, there have been several other exceptional circumstances which have impacted this project. The first was a court case - which included giving a victim statement on behalf of myself and my sister - following the death of my grandfather meaning I spent a prolonged time away from my PhD to be with my family. The second was a diagnosis of Crohn’s and Beçhet’s disease in September 2023 following 9 months of severe symptoms which persisted up until the point of thesis submission, the viva examination, and have continued to impact my life since.

Contributions

Dr Andreas Heinemeyer – Developed the project rationale and acquired funding. Planned the mesocosm site set up and study design. Assisted with mesocosm core collection, installation, and maintenance. Collected some GHG flux measurements and processed all methane fluxes. Assisted with some carbon dioxide flux measurements.

Dr Will Burn – Assisted with mesocosm core collection, installation, and maintenance. Organised permissions for core collection and decided upon site selection. Will found and decided upon the site for the mesocosm storage and designed the rain collection system.

Anthony Jones – Assisted with mesocosm core collection, installation, and maintenance. Ran C:N analysis and assisted with sample preparation for DOC, THM, and HAA analysis. Assisted with mesocosm core collection and mesocosm maintenance. Assisted with GHG flux measurement collection and seasonal porewater collections. Collected vegetation survey data (September 2021) when I was away from PhD study.

Dr Thomas Holmes – Assisted with sample preparation for DOC, THM, and HAA analysis. Undertook some UV analysis (measuring absorbance following chlorination at set time intervals). Assisted with mesocosm core collection and mesocosm maintenance. Assisted with GHG flux measurement collection and seasonal porewater collections. Collected vegetation survey data (September 2021) when I was away from PhD study.

Dr Matthew Pickering – Assisted with method development for THM and HAA analysis. Provided training and guidance for GC/MS analysis and data processing. Processed data for IC analysis.

Mike Beckwith – Assisted with mesocosm core collection.

This project was an iCASE project funded by NERC and the Yorkshire Peat Partnership. An additional 6 months of funding was awarded to allow mitigation for Covid-19 disruption.

List of abbreviations

% C_{org}	Percentage organic carbon
AIC	Akaike information criterion
ANOVA	Analysis of variance
BACI	Before after control impact
BD	Bulk density
C	carbon
C. vulgaris	*Calluna* Vulgaris (also referred to as heather)
CH_4	Methane
C:N	Carbon – nitrogen ratio
CO_2	Carbon dioxide
CUE	Carbon use efficiency
DBP	Disinfectant by-product
DBPFP	Disinfectant by-product formation potential
DEFRA	Department for Environment, Food & Rural Affairs.
df	Degrees of freedom
DOC	Dissolved organic carbon
DON	Dissolved organic nitrogen
E4:E6	Ratio of ultraviolet absorbance at 465 nm and 665 nm
ES	Ecosystem Service
EU	European Union
FTIR	Fourier Transform infra-red
GC - MS	Gas chromatography mass spectrometry
GHG	Greenhouse gas
GLM	General linear model

HAA	Haloacetic acid
He	Helium
HPLC	High performance liquid chromatography
IPCC	Intergovenmental panel for climate change
IR	Infrared
KW	Kruskal Wallis
LCP	Light compensation point
MFF	Moors for the Future
MS	Mass spectrometry
N	Nitrogen
NEE	Net ecosystem exchange
NMDS	Non-metric dimensional scaling
NMR	Nuclear magnetic resonance
NPOC	Non-purgable organic carbon
NVC	National vegetation classification
O_2	Oxygen
OM	Organic matter
P	Phosphorus
PAH	Polyaromatic hydrocarbons
PAR	Photosynthetically active radiation
Peatland ES-UK	Peatland ecosystem services United Kingdom
PLFAs	Phospholipid fatty acids
PMT	Plant mediated transfer
POC	Particulate organic carbon
PVC	Polyvinylchloride

R_{eco}	Ecosystem respiration
RS	Restoration status
Sft	Space for time
SM	Soil moisture
SOC	Soil organic carbon
SOM	Soil organic matter
SR	Soil respiration
SUVA	Specific ultraviolet absorbance
T_{air}	Air temperature
TCM	Trichloromethane (also known as chloroform)
THM	Trihalomethane
T_{soil}	Soil temperature
UK	United Kingdom
UV	Ultraviolet
VIF	Variance inflation factor
WEDOC	Water extractable dissolved organic carbon
WTD	Water table depth
YPP	Yorkshire Peat Partnership
YW	Yorkshire Water

1 Introduction

Peatlands are wetland ecosystems where water-logged conditions give rise to the accumulation of organic matter (OM) and the formation of peat, defined as soil formed solely of OM and normally without a mineral component (Lindsay, 2010a; Zhong *et al*., 2020). Peatland formation, distribution, and carbon (C) storage are controlled by hydrological regime, primary productivity, and OM decomposition rates, all of which are a function of climate (Lindsay, 2010a; Parish *et al*., 2008), vegetation community composition, and the complex interplay of *in situ* soil chemical conditions (Romanowicz *et al*., 2015; Walz *et al*., 2017). Globally, peatlands cover around 3% of the land surface (Parish *et al*., 2008) and are a significant component of the global C cycle (Gorham and Rochefort, 2003), containing around 30% of all terrestrial C stocks (Gorham, 1991; Parish *et al*., 2008). Approximately 13% of the world's blanket bog is found in the UK (Littlewood *et al*., 2010) spanning much of the uplands highly valued for their physical beauty and biodiversity (Reed *et al*., 2009). In more recent times, interest in blanket bog has increased because of their contribution to ecosystem services (ES) (Evans *et al*., 2014), primarily C sequestration (Clay *et al*., 2010) and drinking water provision (Peacock *et al*., 2013; Rosenburgh *et al*., 2013). However, peatlands also produce methane (Abdalla *et al*., 2016), a very potent greenhouse gas (GHG), with emissions generally increasing with higher peat wetness and under warmer conditions (Heinemeyer *et al*., 2019). In the UK, a history of intense management (particularly over the past two centuries) has often led to a reversal in 'active' bog status, and an associated drier peat with a decline in water quality (Peacock *et al*., 2013; Rosenburgh *et al*., 2013b) and C storage (Evans *et al*., 2014). Currently, much needed restoration projects between charity partnerships, non-governmental organisations and government agencies are ongoing, with the aim of identifying best practice management and restoration strategies to reverse and prevent further peatland habitat degradation, thus maximising peatland ecosystem services.

Understanding the impact of various peatland management and restoration practices upon C sequestration, GHG emissions and water quality is imperative to protecting and maximising the benefits of blanket bog ES. Degradation of water quality in peatlands is a significant concern for: GHG emissions due to downstream fluvial dissolved organic carbon (DOC) mineralisation (microbially mediated transformation of OM into gaseous C), the functioning of downstream aquatic ecosystems due to sediment deposition, and for water utility companies due to increased water treatment costs (Martin-Ortega *et al*., 2014a). Chlorination during potable water treatment may result in the formation of harmful disinfection by-products (DBPs) (Gough *et al*., 2016; Xu *et al*., 2018) such as trihalomethanes (THMs) whose concentration in drinking water must not exceed 100 µg L^{-1} and is thus heavily regulated (Peacock *et al*., 2018). High DOC concentrations therefore represent a high cost associated with removal from potable water and penalties for exceeding regulatory guidelines. As a result, water companies are adopting a more holistic approach, focussing on 'treatment at source' rather than at 'end of pipe'. In this approach, a key focus is the role of peatland catchment-scale processes and land management upon drinking water quality (Brooks *et al*., 2015).

Previous work has shown less initial C loss and increased water storage following alternative heather mowing management and higher C and water storage on 'near intact' sites compared to areas under traditional burning practices and more degraded sites. However, the same study showed seasonality in water quality trends but no clear links with heather management (Heinemeyer *et al*., 2019). Other studies have focused largely on linking land management practices with habitat status, overlying vegetation communities, and water table depth (e.g., Worrall *et al*., 2007; Brooks *et al*., 2015). However, there is a current lack of understanding of the underpinning peat chemistry and C decomposition processes which influence C sequestration and peatland water quality. Little is understood regarding how water quality assessments (i.e. UV spectra which can allude OM composition) relate to plant functional types, soil biota, specific organic compounds, and which organic chemical groups are the most significant contributors to peatland catchment DOC issues, and therefore of greatest concern for water companies. Therefore, the key research questions addressed in this thesis are:

1) Does heather management benefit water quality and C fluxes, and can alternative mowing management be used to overcome any effects associated with prescribed burning?
2) Does blanket bog restoration benefit water quality and C fluxes?
3) How will climate change impact blanket bog ecosystem service provisioning?

This project aims to fill these crucial evidence gaps which are currently limiting UK peatland restoration projects and water companies to explain current and predict future trends in C-cycling and links to water quality, and to relate this to habitat status, land management, and climate. The research needs will be addressed through the identification of key chemical plant-soil processes using replicated long-term and catchment-scale evidence alongside controlled short-term mesocosm studies. This project was designed specifically to support organisations such as the Yorkshire Peat Partnership (YPP) and Yorkshire Water (YW) in assessing habitat status, restoration potential, and trajectory towards intact and 'active' blanket bog. Special consideration will be given to plant-soil interactions and the underpinning chemical processes to support maximising the ecosystem services in relation to carbon storage, climate regulation and water quality provided by blanket bogs.

Project aims

This project will investigate peat chemical and physical properties and link them to management regime, habitat status, and climate. The project aims to provide answers to the key practitioner question of: **Which blanket bog vegetation community, habitat status and management regime is best in relation to C-storage, DOC compounds affecting water quality and the main GHG emissions (i.e., carbon dioxide and methane)?**

The subsidiary aims are to:

1) Assess water quality and greenhouse gases fluxes in peat soils under prescribed burning, mowing, and nil-management management regimes.
2) Assess water quality and greenhouse gas fluxes in peatland soils of 'degraded' and 'intact' status and following restoration.
3) Assess the impact of climatic conditions on water quality and the main GHG fluxes in peatland soils.
4) Assess how comparable findings from controlled mesocosm studies are to long-term field studies.
5) Investigate water quality parameters and disinfectant by-product formation in peatland soils.

This thesis therefore contributes knowledge to unanswered questions in peatland science through the successful completion of the following objectives:

1) **To ascertain whether alternative mowing vegetation management is beneficial to porewater quality and greenhouse gas fluxes**. Mowing heather management offers an alternative to the controversial prescribed burning management regime. The hypothesis that '*alternative mowing management with higher water tables benefits peat water quality compared to prescribed burning'* was tested. Peat pore water samples were taken from a controlled peat mesocosm study comparing recovery after previous burning or mowing of heather to no heather management.
2) **To ascertain whether habitat/restoration status is reflected in porewater quality and if water quality parameters and chemical groups can be used to test the recovery and trajectory of restored sites**. Blanket bog restoration is undertaken in an attempt to reverse the impacts of degradation largely resulting from ill-informed management practices. The hypothesis that '*restoration improves water quality parameters and*

indicator functional groups translate to habitat status which can be used to test recovery and trajectory status of restored sites' was tested. Seasonal porewater sampling and carbon flux measurements undertaken in mesocosm cores from degraded, intact, and restored sites were used to assess restoration trajectory.

3) **To ascertain whether water quality and greenhouse gas fluxes vary with climatic conditions and how blanket bog ecosystem service provisioning may be affected in the context of climate change**. Climate change is projected to cause a destabilisation of soil C-stocks if effective mitigation strategies are not put in place. The hypothesis that '*water quality is better from wetter, cooler and more intact sites representing slower C turnover and larger C storage'* was tested. Seasonal porewater sampling and GHG flux measurements were taken from mesocosm cores collected from a climatic and habitat condition gradient across UK blanket bogs.
4) **To ascertain whether mesocosm samples provide meaningful ecological information compared to field studies**. There remains large uncertainty in how meaningful findings from mesocosm studies are as artefacts could result in altering C cycle processes and thus limit generalisation of results. The hypothesis that '*mesocosms provide comparable data to field observations in relation to C cycle processes and water quality when accounting for differences in environmental factors*' was tested. Seasonal porewater sampling and GHG flux measurements was undertaken in heather management mesocosm cores and results were compared to in-situ measurements taken at the original peatland mesocosm locations.
5) **To ascertain whether disinfectant by-product formation potential of soil porewaters varies with management regime, restoration status, and climatic conditions.** Increased DOC loading of waters entering water treatment works is problematic for utility companies who are relying on chemical treatment methods**.** The hypothesis that '*water samples with greater colour (UV absorbance) will have a higher disinfectant by-product formation potential but will be more amenable to water treatment'* was tested. Management and restoration effects on water quality samples from mesocosms were assessed in the context of minimising drinking water treatment costs.

Thesis structure

This thesis includes four main data chapters. Work undertaken to address the project aims and objectives is presented in these data chapters, after this overall introduction (**Chapter 1**) to the thesis and an introductory literature review and culminates in overall conclusions which summarise the main findings from each chapter and considers these results in a wider context.

Chapter 2 is a literature review which summarises the importance of UK blanket bog ecosystems along with key components and drivers of peatland soil C cycling and associated ecosystem services. This chapter discusses the current knowledge gaps in peatland science.

Chapter 3 is a methodological outline which provides site descriptors, mesocosm site set up, and sampling and analytical methodology, with water quality testing and GHG flux measurement methodology relevant to chapters 4-6 and water quality measurements and disinfectant by-product formation GC-MS methodology relevant to chapter 7.

Chapter 4 assesses the impacts of management regimes on blanket bog water quality and GHG fluxes. Water quality and C fluxes (i.e. CO_2 and methane) were compared for mesocosm cores sampled from three blanket bog areas, each with a sub-set of site mesocosms from either prescribed burning, alternative mowing or a nil-management regime.

Chapter 5 assesses blanket bog restoration practices in the context of water quality and GHG fluxes. Water quality and C fluxes were compared for mesocosm cores sampled from three climatically different blanket bog areas , each with a sub-set of site mesocosms classified as either 'near intact', degraded or post- restoration.

Chapter 6 assesses the impacts of climate upon blanket bog water quality and GHG fluxes. Water quality and C fluxes were compared in mesocosm cores sampled from four blanket bog regions. This chapter combines data from samples collected as part of chapters 4 and 5.

Chapter 7 assesses disinfectant by-product formation in blanket bog porewaters from areas under the various management regimes, habitat and restoration statuses (discussed in chapter 5), and climatic regions. Samples utilised in chapters 4-6 were analysed in this chapter.

Chapter 8 summarises the main thesis findings and makes recommendations on management and restoration strategies based on conclusions made in previous chapters. Suggestions for further work to address identified knowledge gaps are also given.

2 Literature review

2.1 Introduction to peatlands

Peatlands are wetland ecosystems whose soils are without a significant mineral component. Globally, they represent an important terrestrial C store, with some estimates being akin to the C pool stored in the global vegetation stock (Table 2.1; Lindsay, 2010a; Zhong *et al*., 2020; Parish *et al*., 2008; Romanowicz *et al*., 2015; Walz *et al*., 2017). They are most abundant across northern mid to high latitudes, with their formation tailing the retreating ice sheets following the end of the last glaciation (Loisel *et al*., 2017) due to increased plant biomass production during warmer periods (Yu *et al*., 2010). Since this time (i.e., the Holocene), they have accumulated an estimated 600 Pg C (Frolking and Roulet, 2007). Whilst so far, northern peatlands have exhibited an overall negative radiative impact upon the climate, under projected global changes, peatland C pool stability is uncertain (Loisel *et al*., 2017).

Table 2.1 Estimated mass of carbon stores in various carbon sinks reported within the literature (1 Pg = 10^{15} g).

Carbon sink	Estimated mass of total carbon store (Pg)	Reference
Boreal and Sub-Arctic peatland soil organic matter	250-547	Frolking and Roulet (2007); Gorham (1991); Turunen *et al* (2002); Yu *et al*., (2010)
Global vegetation carbon stock	550	Houghton (2007)
Tropical peatlands soil organic carbon	82-92	Page *et al* (2011)
Atmospheric carbon	780	Houghton (2007)

In the UK, peatlands have undergone many centuries of management (such as drainage, grazing of livestock, and prescribed burning), primarily driven by cultural and economic factors (Reed *et al*., 2009). As a result, many UK peatlands are severely degraded due to what some consider to be irreversible changes in hydrological and soil properties (Holden *et al*., 2007). In recent times, interest in peatland restoration has increased (Gorham and Rochefort, 2003), particularly in the UK uplands, to maximise the potential of the ES peatlands provide. In the UK, blanket bog peatland is a prominent upland habitat and has been subject to extensive scientific investigation. However, scientific uncertainty surrounding the effects of various upland land management practices on water provision and quality, C accumulation, and climate change mitigation has hindered a definitive consensus being reached on how best management practice. UK blanket bog is therefore the focus of this study.

2.1.1 Global Blanket Bog Characteristics

Blanket bog – named for their blanketing of the underlying bedrock with peat (Everett, 1983; Lindsay, 2010a) - dominates much of the UK uplands, comprising 22,500 km^2 of the total 29,000 km^2 UK peat cover (Bain *et al*., 2011; Holden *et al*., 2004). Their surface is a mosaic of undulating microforms, often consisting of alternating raised hummocks and low hollows (Grand-Clement, 2008; Heinemeyer *et al*., 2019), which exhibit differences in water table depth, overlying vegetation composition, and pH (Laine *et al*., 2006). Blanket bog soils are ombrotrophic (exclusively 'rain fed'), averaging 1-4 m in depth, and are nutrient poor because of being isolated from underlying groundwater, unlike groundwater-fed peat fen (Lindsay, 2010). In this work, blanket bog and peatland are used to refer to upland ombrotrophic mire only, and fen peatlands are not considered as part of this thesis.

Similarly to other types of peatlands, blanket bog can be characterised by two distinct zones (Figure 2.1): the mostly unsaturated aerobic acrotelm and the saturated anaerobic catotelm (Ingram, 1978). The acrotelm, situated just below the peat surface, is typically 10-20 cm in depth (Lindsay, 2010a) and consists of living plant material and relatively uncompacted organic material (Grand-Clement, 2008). Biomass production occurs in the acrotelm via litter input from photosynthesis (Shiller, 2013), thus increasing the peatland C pool. Decomposition rates are higher here than in deeper peat due to the presence of oxygen and aerobic microbes (Clymo, 1984; Kuder and Kruge, 2001). Beneath the acrotelm is the permanently saturated catotelm which is an anaerobic layer characterised by lower hydraulic conductivity. The catotelm receives partly decayed OM from the acrotelm, but also fresh root C inputs (e.g. from deep rooting sedges). Long term C storage occurs in the catotelm due to oxygen limitation and a subsequent slow rate of OM degradation (Clymo, 1984; Kuder and Kruge, 2001). Because of water table fluctuations, there is a periodically saturated mesotelm situated between these two layers (Clymo and Bryant, 2008). This zone model is considered a simplification of a more complex hydrology, and the transition from an oxic to anoxic zone is unlikely to occur over a single boundary. However, this model is a useful approximation and is frequently utilised by peatland soil organic matter (SOM) models (e.g. the MILLENNIA peat cohort model Heinemeyer *et al*., 2010 and the LORCA model Turunen *et al*., 2002).

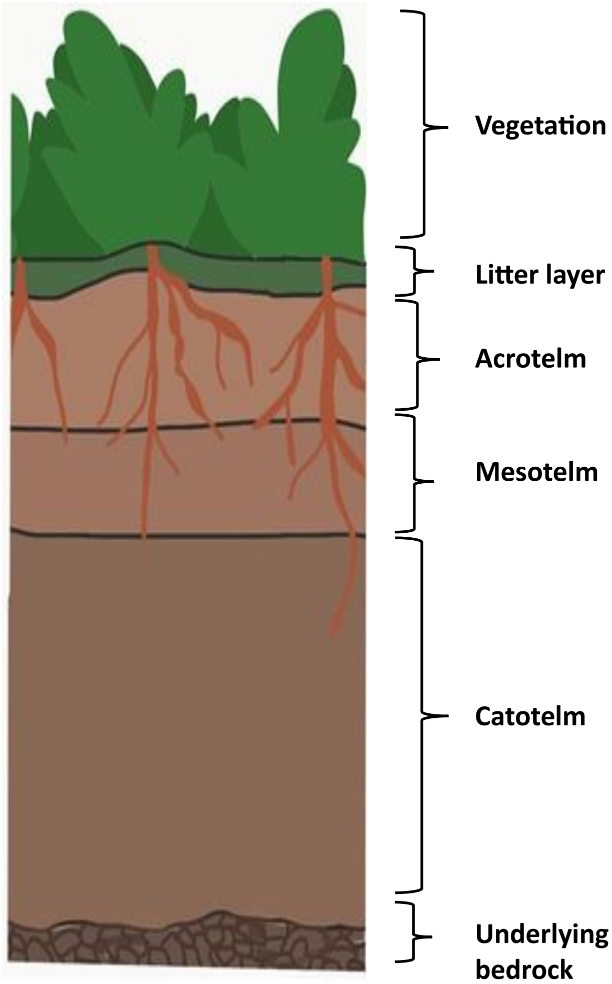


Figure 2.1 Schematic drawing of the acrotelm-mesotelm-catotelm peatland hydrological model.

2.1.1.1 Blanket bog vegetation

As a result of a poor nutrient status, blanket bogs support a unique plant assemblage (Thompson *et al*., 1995) which varies with bog topography due to variations in hydrological condition (Table 2.2) (Lindsay, 2010a). 'Active' blanket bog, assumed to accumulate peat (Maddock, 2008), is dominated by M1, M2, M3, M15, M17, M18, M19, M20, and M25 National Vegetation Classification (NVC) types (elaborated in Table 2.2) (Maddock, 2011) whereas more degraded ('inactive') blanket bog may be dominated by dry heath vegetation. However, the distinction of 'active' vs. 'inactive' or degraded bog, although often used (e.g. Flynn *et al* (2015)), seems not to be based on robust evidence (Ashby and Heinemeyer, 2021). As C is sequestered even under intense burn rotation management (Heinemeyer *et al*., 2018; Marrs *et al*., 2019), a more useful distinction might be based on modification status (i.e., more or less modified) in relation to overall habitat condition and vegetation.

A vegetation community composed largely of *Sphagnum* is considered desirable in maintaining 'active' bog conditions. *Sphagnum* mosses are thought of as a key 'peat forming' species and are considered pivotal for blanket bog ecosystem functioning, influencing hydrology, chemistry, and C sequestration (Noble *et al*., 2019, 2018a). They produce peat with a high cation exchange capacity and thus a lower pH than sedge-formed peats (Mitsch and Gosselink, 2015). In this acidic environment, *Sphagnum* are highly resistant to decomposition (Abbott *et al*., 2013). However, clear separation between *Sphagnum* species in relation to their environmental niche (i.e., water and nutrient levels) is often rather vague when looking at the main underpinning study (Daniels and Eddy, 1985). Moreover, the claim of 'peat-forming' species, although frequently referred to (e.g. Norby *et al*., 2019; Bengtsson *et al*., 2021) has more recently been contested (Heinemeyer and Ashby, 2021). Noticeably, it is predominantly environmental conditions (i.e. temperature pH, hydrology, nutrients) rather than the species which determines peat formation (Davidson and Janssens, 2006), but *Sphagnum* moss facilitates such conditions.

Table 2.2 National Vegetation Classification (NVC) types of 'active' blanket bog vegetation species.

National Vegetation Classification	Plant community/sub-community name	Reference
M1	*Sphagnum auriculatum* bog pool community	Rodwell (2006)
M2	*Sphagnum cuspidatum/recurvum* bog pool community	
M3	*Eriophorum angustifolium* bog pool community	
M15	*Scirpus cespitosus-Erica tetralix* wet heath	
M17	*Scirpus cespitosus-Eriophorum vaginatum* blanket mire	
M18	*Erica tetralix-Sphagnum papillosum* raised and blanket mire	
M19	*Calluna vulgaris-Eriophorum vaginatum* blanket mire	
M20	*Eriophorum vaginatum* blanket and raised mire	
M25	*Molinia caerulea-Potentilla erecta* mire	

2.2 Peatland carbon

Peat soils are a heterogeneous mixture of plant, animal, and microbial derived organic compounds (Ussiri *et al*., 2003), and unlike mineral soil systems, are characterised by a very high OM content

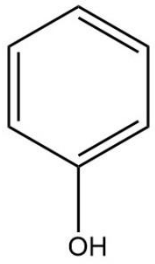
(Lindsay, 2010b). Soil organic matter (SOM) is subject to biological, physical, and chemical mediated processes, dependent upon soil conditions (temperature, redox conditions, pH) and OM chemical composition (Lehmann and Kleber, 2015; Schellekens *et al*., 2009).

2.2.1 Peat organic matter chemical composition

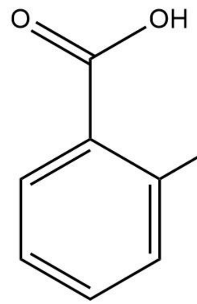
Peat OM chemical composition is highly variable and is a function of climate, habitat status, degree of decomposition, site hydrology (Chapman *et al*., 2001), and the solubilisation and transport of OM within the soil profile (Ussiri *et al*., 2003). Organic molecules range from recalcitrant macromolecules such as lignin to smaller, more easily degraded compounds such as amino acids and consists of both aliphatic and aromatic compounds which can be hydrophilic or hydrophobic (Kögel-Knabner, 1997). OM structure and complexity has implications for C sequestration and water treatment, which in the context of blanket bogs, has been the subject of recent increased interest. In the following section the chemical properties of the main chemical groups within peat OM are discussed along with their role in C gaseous fluxes (Section 2.2.3 and implications for water quality and treatment (Section 2.7).

2.2.1.1 Phenolics

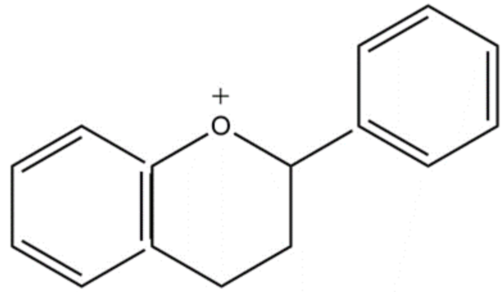
Phenolics are a diverse class of chemical compounds consisting of a hydroxyl functional group bonded directly to an aromatic hydrocarbon group consisting of six C atoms. Phenolics found in peat soils encompass constituents of ligno-humic complexes and lower molecular weight compounds such as phenolic acids, flavonoids, lignans, and unhydrolysable substances such as tannins and stilbenoids (Figure 2.1) (Naumova *et al*., 2013). In soils, they are derived from plant metabolites and are important in plant pigmentation, growth, reproduction, and pathogen resistance (Abbott *et al*., 2013). Due to relatively slow decomposition rates, they are important regulators in soil decomposition processes and are thus crucial in both peat formation and long-term C sequestration (Freeman *et al*., 2001).



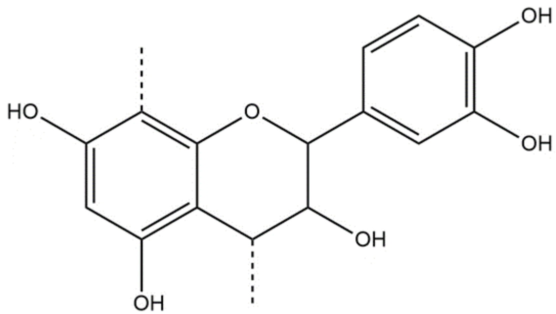
Phenol



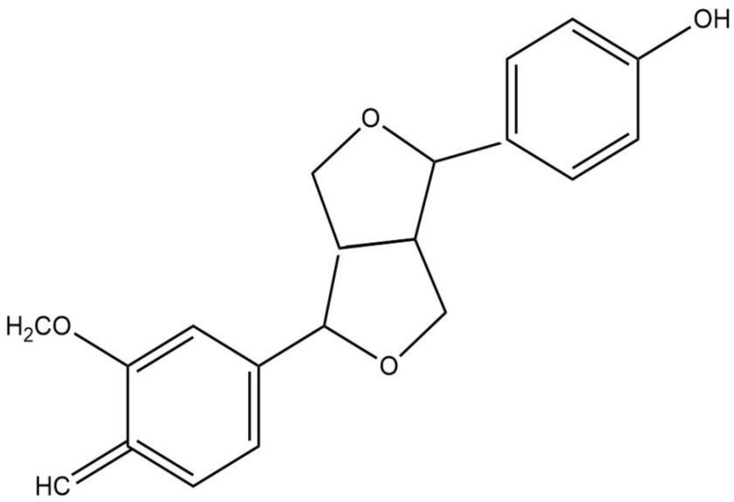
Phenolic acid



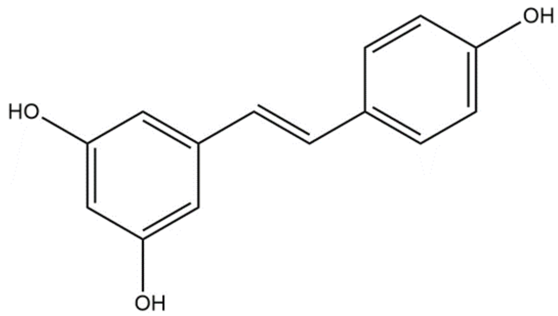
Flavonoid



Tannin



Basic lignan unit



Stilbenoid

Figure 2.2 Examples of phenolic compounds found in peat.

The breakdown of phenolic compounds within soils occurs enzymatically through microbially-produced phenol oxidases (Burke and Cairney, 2002; Williams *et al*., 2000) which are among the few enzymes able to wholly degrade phenolic compounds (Limpens *et al*., 2008; Dunn and Freeman, 2018). Phenol oxidase suppresses the activity of hydrolase enzymes - the primary agents of C and nutrient cycling - thus preventing the decay of SOM (Freeman *et al*., Kang, 2001). Extracellular phenol oxidase activity is affected by site-specific factors including oxygen, soil moisture, nutrient availability, and chemical inhibitors (Bonnett *et al*., 2017) and is abundant in peatland soils due to low oxygen availability in much of the soil profile, low temperatures, and low pH (Limpens *et al*., 2008). A theory has been proposed that a perturbation in just one of these properties could release an "enzymatic latch mechanism" (Freeman *et al*., 2001) resulting in the destabilisation of peatland C storage via the breakdown of otherwise highly recalcitrant OM and indirectly via releasing extracellular hydrolase enzymes from phenolic inhibition (Limpens *et al*., 2008).

Sphagnum litter has a slow decomposition rate which is attributed to an abundant phenolic, species-specific macromolecule containing ρ-hydroxy-β-[carbixymethyl]-cinnamic acid (Figure 2.2), commonly referred to as *Sphagnum* acid (Schellekens, 2013). It is present in hyaline cell walls providing structural support and inhibits microbial decomposition of cell wall polysaccharides. *Sphagnum* derived phenols are preferentially lost during aerobic decay within the acrotelm, and subsequently their decomposition is intrinsically linked with water table depth (Abbott *et al*., 2013; Schellekens *et al*., 2015a).

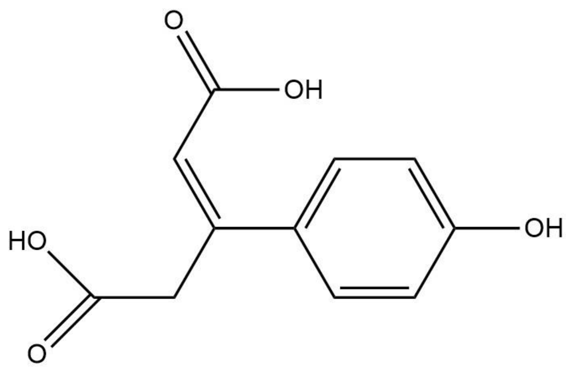


Figure 2.3 Schematic of the molecular structure of ρ-hydroxy-β-[carbixymethyl]-cinnamic acid (Sphagnum acid).

2.2.1.2 Lignin

Lignin is a phenolic polymer (Hedges and Ertel, 1982) consisting of aromatic rings with side chains and -OH and -OCH_3 groups linked by strong covalent bonds (alkyl-aryl ether and C-C; Figure 2.3)

(Thevenot *et al*., 2010). It is the most abundant aromatic terrestrial vascular plan component and the second most abundant plant component after polysaccharides (Thevenot *et al*., 2010; Derenne and Largeau, 2001). It is particularly abundant in higher plant cell walls (Schellekens, 2013) where it is chemically connected to cellulose and hemicellulose providing rigidity and strength, and resistance to enzymatic hydrolysis (Thevenot *et al*., 2010). It is one of the most recalcitrant of plant residues (De Deyn *et al*., 2008) because of its aromaticity and diversity of its chemical bonds, and thus accumulates in soils (Derenne and Largeau, 2001; Sollins *et al*., 1996). Lignin exhibits a greater degree of resistance to microbial degradation in comparison to polysaccharides and amino acids (Jex *et al*., 2014), but in the acrotelm it can be degraded aerobically, for example, by white-rot and brown-rot fungi (De Deyn *et al*., 2008). In the catotelm however, due to the specificity of lignin degradation enzymes and the limited abundance of the soil fungi which produce them, lignin has a long soil residence time and persists with depth, making it significant for long term soil C sequestration (De Deyn *et al*., 2008).

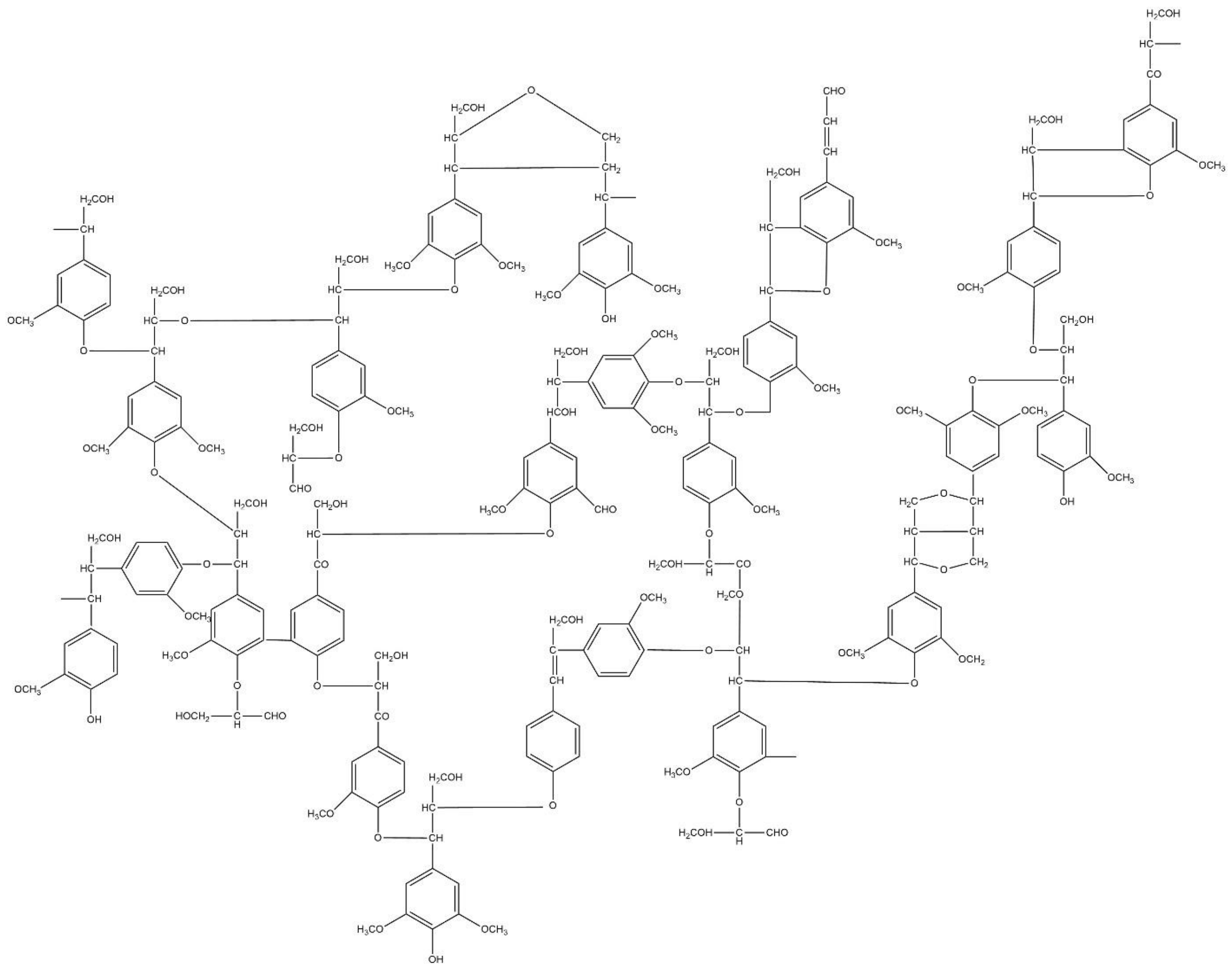
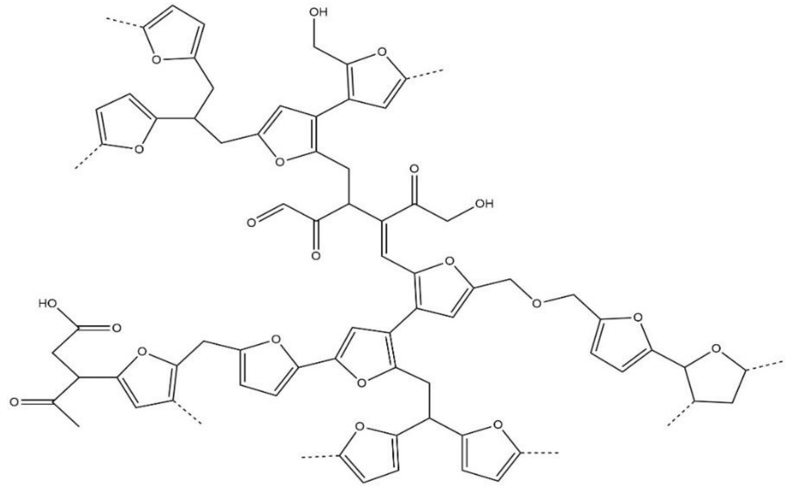


Figure 2.4 Schematic of the molecular structure of lignin (Watkins *et al.*, 2015).

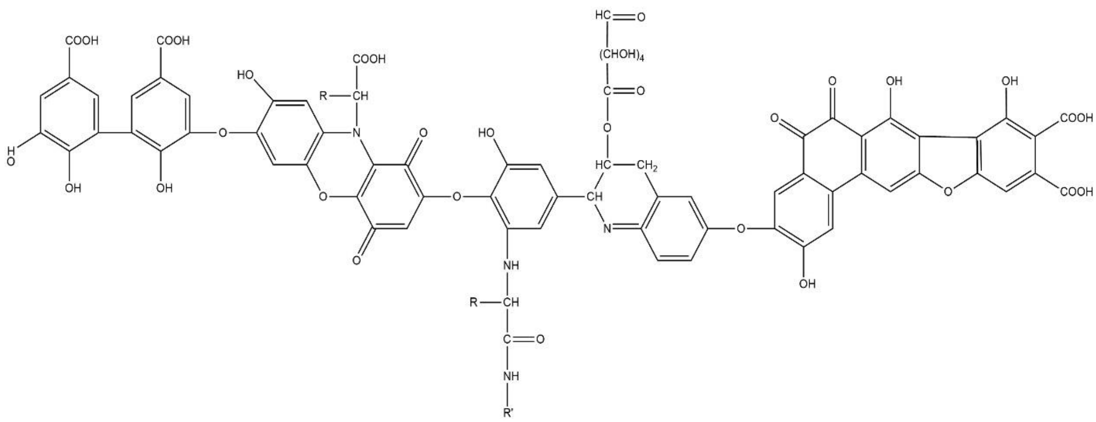
2.2.1.3 Humic substances

Humic substances are the most abundant organic substances in peat and natural waters. They are naturally occurring, heterogeneous, generally yellow to black in colour, of high molecular weight (≤ 1000 daltons) and are relatively recalcitrant to decomposition (Dudare and Klavins, 2013; Klavins and Purmalis, 2008). Humic substances contain a large number of functional groups, including but not limited to -COOH, -OH (phenolic and aliphatic hydroxyl), $-CH_2$, -O-, and -NH- (Dudare and Klavins, 2013) and can be split into three fractions: **a**) humin which is not soluble at any pH; **b**) humic acid which is not soluble under acidic conditions (< pH 2) but is soluble at higher pH; and **c**) Fulvic acid which is soluble at any pH (Figure 2.6) (Klavins and Purmalis, 2013).

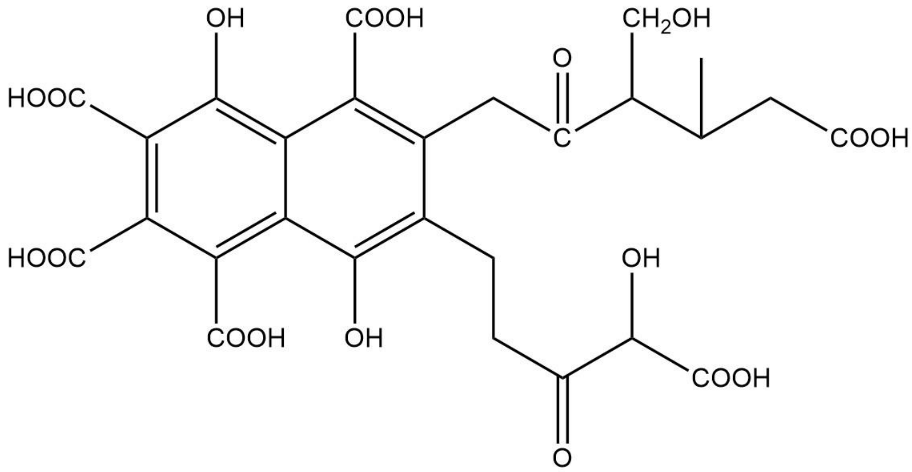
In peat soils, microbial activity is the primary driver of decomposition processes of which humic substances are by-products (Yallop and Clutterbuck, 2009). Humic material composition can be linked to diagenetic processes, and is therefore reflective of parent material, climate conditions, and habitat status. Humic material is pivotal in determining soil chemical properties – buffer capacity, acid-base reactions, and cation exchange capacity (Gondar *et al*., 2005) – and thus is an important component of organic-rich peat soils.



Humin



Humic acid



Fulvic acid

Figure 2.5 Schematic of the molecular structure of the three fractions of humic substances within peat: a) humin b) humic acid and c) fulvic acid.

2.2.1.4 Lipids

Lipids are a major constituent of OM, predominantly forming part of the structural components in cuticular waxes in higher plants and cell membranes (e.g. phospholipids) and acting as energy stores (e.g. triglycerides) (Younes and Grasset, 2018) . They are insoluble in water because of their non-polarity and are characterised by their solubility in organic solvents rather than structural characteristics. The term ‘lipid’ encompasses a variety of compounds including but not limited to fats, waxes, steroids, terpens, phospholipids, pigments, alkanes, polycyclic aromatic hydrocarbons (PAHs), and resins (Table 2.4).

Lipids in peat soils originate largely from plant material with only a small portion deriving from microbial activity (Moucawi *et al*., 1981). Their degradability is dependent upon chemical complexity: long-chain aliphatic fatty acids and phospholipids are more rapidly degraded in soils- as degradation rate is dependent upon the degree of saturation- whereas more complex lipids such as cutin and suberin are more recalcitrant, sorbing onto hydrophobic components of OM, resisting biological decomposition. In addition to chemical structure, lipid decomposition rates within soils is also dependent upon soil biological activity (Moucawi *et al*., 1981).

Peatland vegetation produces distinctive C chain length distributions of lipids (Table 2.5), and therefore the lipid characterisation within peat sequences can provide insight into evolution of overlying plant communities and any perturbations affecting peat soils post-deposition (Zhang *et al*., 2017). Moreover, phospholipid fatty acids (PLFAs) are commonly used to characterise the soil microbial communities (Bragazza *et al*., 2012).

Table 2.3 Characteristics of lipids found in peat soils.

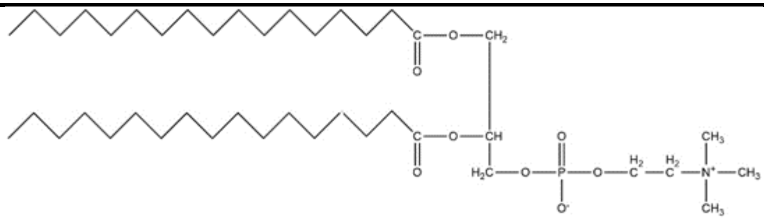
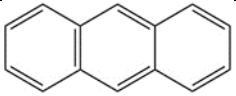
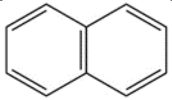
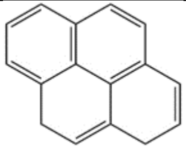
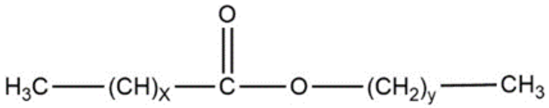
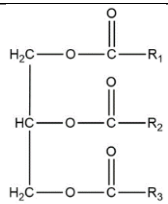
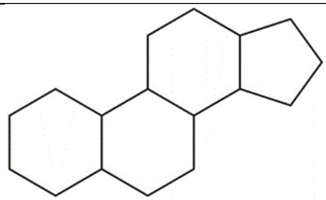
Lipid	Examples of molecular structure	Properties	Reference
Phospholipids		Consists of a hydrophilic polar head and a hydrophobic tail. The polar head contains >1 phosphate group (PO_4^{3-}). When in solution, they form a bilayer.	
Polycyclic aromatic hydrocarbons (PAH)	 Anthracene  Naphthalene  Pyrene		
Waxes		Long chain carboxylic acids with long chain alcohols. Usually saturated and contain an even number of carbon atoms. (x = 24,26 and y=29,31).	Parsons (2003)
Fats		Triglycerides which form glycerol and three carboxylic acids (fatty acids) upon hydrolysis. Side chains in fatty acids can be saturated or unsaturated and contain between 12 and 20 carbon atoms.	
Steroids		All contain one cyclopentane ring, and three cyclohexane rings which are all linked.	

Table 2.4 Lipid characteristics associated with peatland vegetation. Adapted from Zhang *et al* (2017).

Lipid characteristic		Vegetation type	Reference
***n*-alkanes**	Mid-chain (C_{23} and C_{25})	*Sphagnum* spp. and floating aquatic vascular plants	Bingham *et al* (2010)
	Long chain (C_{27}, C_{29} and C_{31})	Terrigenous higher plants	
***n*-fatty acids**	Short chain (C_{14}, C_{16}, C_{18})	Aquatic algae and bacteria	Cranwell (1973)
	Long chain (C_{24}, C_{26}, C_{28})	Terrigenous higher plants	

2.2.1.5 Polysaccharides

Polysaccharides in peatland soils are of plant and microbial origin (Kögel-Knabner, 2000) , constituting the majority of peat OM along with phenolic compounds (D'Andrilli *et al*., 2010) as they are a major component of plant cell walls (Jones *et al*., 2003) . There is a preferential loss of polysaccharides over lignin in peat soils and along with carbohydrates (largely due to single bond hydrocarbon chains; Figure 2.5), they are most readily removed from the SOM pool in the initial stages of OM decomposition (Worrall *et al*., 2017)..

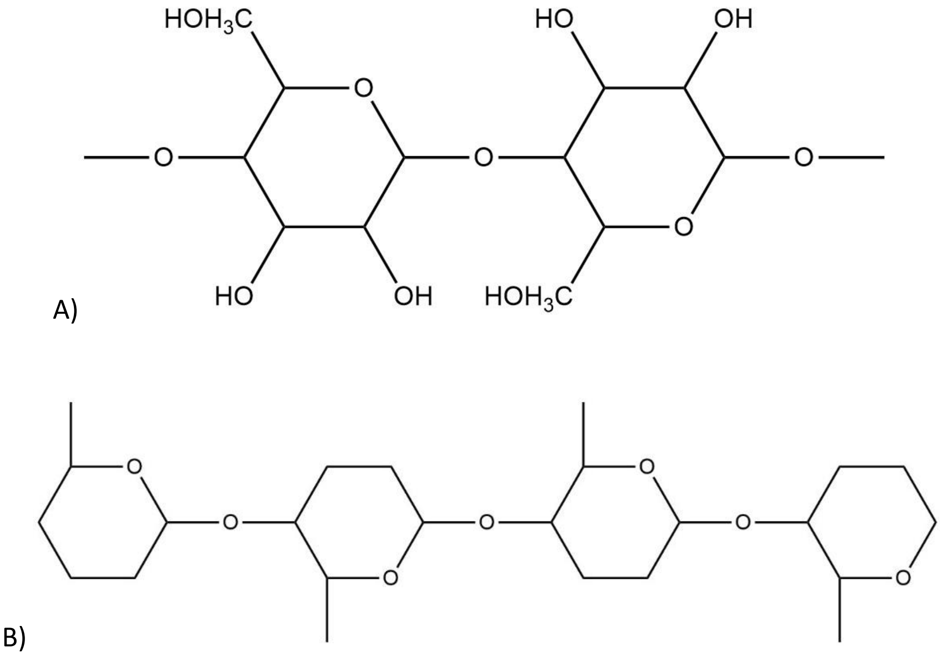
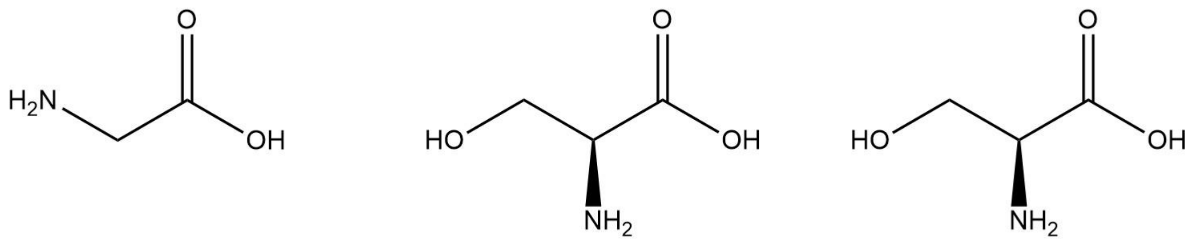


Figure 2.6 Molecular structure of two polysaccharides: A) Cellulose, and B) β-glucose.

2.2.1.6 Proteins and amino acids

Amino acids and peptides are a source of both C and N in peatlands and form the majority of organic N within soils. They are components of humic acids where they exist as insoluble N and amino acids bound in peptides, whereas the free amino acid pool is very small. The amino acids present within soils reflect the composition of overlying vegetation communities. The dominant amino acids which constitute >5% of the total amino acid pool are glycine, serine, aspartate, glutamate, threonine, alanine, valine, proline and leucine (Figure 2.8) (Scarpelli, 2016).



Glycine **Serine** **Aspartate**

Figure 2.7 Examples of amino acids most commonly found in peatland soils. Adapted from Scarpelli (2016).

Plants are around 10-30% protein by weight and amino acid concentration is generally ~10 mM (Jones, 1999). Amino acids are released as exudates from plant roots where they may be utilised by microbes and plant roots within the rhizosphere or transported in response to diffusion, mass flow, and within solution in soil pore water (Jones, 1999). Soil amino acids are assumed to be largely microbial in origin given that significant amounts of amino sugars are not synthesised by plants (Roberts *et al*., 2007). They are a major component of fungal and bacterial cell walls and unlike other abundant low molecular weight soil compounds, most amino acids enter the soil upon organism death (Roberts *et al*., 2007).

Amino acids are removed from soils by extracellular enzyme activity which break down amino acids to monomers where they may undergo: 1) soil microbial biomass uptake; 2) plant root uptake; 3) abiotic mineralisation, and 4) leaching down the soil profile (Roberts *et al*., 2007) Amino acids derived from proteolysis - the breakdown of proteins into amino acids or polypeptide - and other monomers may form larger, more complex, recalcitrant molecules during protein depolymerisation and re-condensation processes (Scarpelli, 2016). Whilst amino acid decomposition in peat soils has not been extensively studied, behaviour in mineral soils may provide some insight into amino acid breakdown in organic soils. In mineral soils, amino acid decomposition is rapid with half-lives of 1-12 hours depending upon chemical and physical soil characteristics and environmental conditions (Jones, 1999) . Amino acid availability to and uptake by peatland vegetation and soil microbes is likely to be impacted by climate change (Scarpelli, 2016) which may have implications for peatland C cycling processes.

2.2.1.7 Organic matter composition and depth

OM composition in peatlands varies with depth as electron transfer processes proceed in a vertically structured environment (Limpens *et al*., 2008) . Reduced compounds produced during primary production buried as litter or as root exudates induce a redox gradient to the soil surface. As a result, oxygen diffusion, advection, and aerenchymatic transport within roots influence soil oxygen availability (production and consumption). This redox gradient induces four important vertical trends within the peat soil column: 1) The importance of root respiration versus heterotrophic respiration decreases with depth as roots are largely constrained to the upper peat layers (Heinemeyer *et al* 2011); 2) Litter degradability decreases with depth as a result of the production of more decomposed and recalcitrant residues (Heinemeyer *et al*., 2010) ; 3) Gas and solute transport decreases due to a decline in hydraulic conductivity with depth due to increased saturation and compaction (Holden *et al*., 2014) ; and 4) Electron acceptors are depleted rapidly in the catotelm and therefore decrease with depth (Limpens *et al*., 2008) . As a result, OM degradation largely occurs in the acrotelm and degradation products are buried in the catotelm and thus SOM composition varies and shows an overall increasing OM recalcitrance with depth: readily degradable OM (e.g. oxygen-rich compounds such as hydrophilic polysaccharides) is lost preferentially leaving a more recalcitrant organic fraction (i.e. lignin, polyphenols and hydrophobic aliphatic microbial products) in the deeper peat. This leads to a reduction in soil respiration with depth, as demonstrated with incubated peat cores (Kleber, 2010; Leifeld *et al*., 2012) . Current understanding is that carbohydrates, carboxyl-C and oxygenated functionalities decline whilst aliphatic-C, aromatic C, and microbial mucilage increases with depth, which is likely to be related to recalcitrance .

2.2.2 Peatland carbon cycling

Peatlands play a significant role in the global C cycle owing to their ability to sequester and store C long-term (Robroek *et al*., 2010) . Historically, they have been reported to exhibit a net ‘cooling’ effect upon the climate (Frolking *et al*., 2006) based on their assumed general negative GHG emissions. C sequestration in peatlands occurs where net primary productivity (NPP) exceeds the rate of SOM decomposition, leading to the deposition of partly decomposed OM and the formation of peat (Clay *et al*., 2010b). ‘Active’ peatland is therefore seen to act as a net C sink and is of potentially a major importance for controlling atmospheric CO_2 emissions (Billett *et al*., 2006)(Billett *et al*., 2006)(Billett *et al*., 2006) and are estimated to have an average long-term C accumulation rate of ~30 g C m^{-2} yr^{-1} (Gorham, 1991) . Peatlands normally act as C sinks for millennia, but when damaged and disturbed, can act as C sources, releasing large amounts of CO_2 gas into the atmosphere and DOC into fluvial systems (Kayranli *et al*., 2010; Limpens *et al*., 2008; Shiller, 2013) . Whether peatlands will continue to be C sinks depends upon the impact of anthropogenic and environmental forcing upon the C balance (Limpens *et al*., 2008) .

Peatland C sequestration and decomposition are intimately linked with land management, climate (Clay *et al*., 2010b) , and soil conditions (Kuder and Kruge, 2001) . Land management strategy and climate both affect water table depth (WTD), which is the driving factor controlling peat ecosystem processes (Bonnett *et al*., 2017) . A deep-water table exposes more of the peat column to oxic conditions, leading to increased litter decomposability, heterotrophic respiration, and hydrological conductivity within the acrotelm and thus a general decline in long term C sequestration (Limpens *et al*., 2008) . Blanket bog vegetation distribution is also influenced by water table depth as a decrease in wetness can stimulate a shift from a *Sphagnum*-dominated vegetation type to vascular plants (Limpens *et al*., 2008) . As the biochemistry of vascular plants and mosses varies greatly, soil litter C inputs will change (Abbott *et al*., 2013) .

OM composition and decomposition processes are largely a function of plant and microbial residues and their transformation products (Kögel-Knabner, 2000) . Microbial OM decomposition is a function of nutrient and electron acceptor availability which is affected by soil physical structure and overlying vegetation community, and the availability and activity of extracellular enzymes (Limpens *et al*., 2008) . In an anoxic environment-such as in the catotelm- oxidative capacity is stored in the form of nitrate, ferric iron hydroxides, sulfate, and humic substances in heterotrophic respiration. Gibbs free energy determines which chemical species is utilised by the microbial community along with electron acceptor and donor concentration (Limpens *et al*., 2008).

The composition of peat SOM reflects bog hydrological status (affecting C decomposition) and overlying vegetation (C input; Table 2.6 and Table 2.7) composition (Schellekens, 2013; Schellekens *et al*., 2015b) . Vegetation sequesters atmospheric C via photosynthesis, with a fraction of this converted to glucose, ultimately forming plant components such as lignin, carbohydrates, proteins, and lipids, and following plant death, returned to the SOM pool (Frolking *et al*., 2006) . At local ecosystem levels, the C balance is influenced by plant litter due to differences in productivity, litter decomposability and microbial associations with consequential vegetation-biochemistry feedbacks (Limpens *et al*., 2008).

Table 2.5 Distinctive chemical composition of typical blanket bog vegetation.

Vegetation	Distinctive chemical composition	Reference
***Sphagnum* spp.**	High phenolic content	Schellekens *et al* (2015b)
Lichen	Polysaccharides	Schellekens *et al* (2009)
Calluna	Lignin Polyphenols	Abbott *et al*., (2013)
Moss	No lignin.	
Litter	Reflective of originating vegetation.	Farmer and Morrison (1964)

Table 2.6 Composition of organic matter reservoirs within blanket bog using thermogravimetric analysis. Adapted from Worrall *et al* (2017).

Organic Matter Reservoir	Composition (%)		
	Cellulose	Lignin	Protein
C. vulgaris	36	64	0
Sedges and grass	74	23	3
Mosses	61	24	15

SOM decomposition is a function of biogeochemical processes regulated by soil fauna and microorganism activity, the transport of electron acceptors and nutrients, and the quality of OM inputs (Limpens *et al*., 2008) . The concept of OM quality is linked to litter decomposition-based peatland soil organic carbon (SOC) models (Bauer, 2004; Heinemeyer *et al*., 2010) and refers to the required number of enzymatic steps to release a C atom from an organic molecule in the form of CO_2. Lower quality SOM requires more enzymatic degradation steps and thus a higher activation energy (Kleber, 2010). OM groups such as lignin are recalcitrant and not easily broken down in peat soils, and thus represent a potential long-term C store. Microbial extracellular enzymes have an important function in enhancing decomposition processes (Bonnett *et al*., 2017), breaking down complex molecules to simple monomers which are utilised by soil biota. In peatlands, a potentially important, but so far understudied, group are mycorrhizal fungi, which obtain C from their host plant in return for nutrient acquisition, enhanced via special enzyme capabilities (Read, 1991). Environmental conditions can affect these enzymes and subsequently soil microbial communities through changes in temperature, nutrient availability, electron acceptors, and soil physical structure (Limpens *et al*., 2008). Soil moisture also affects enzyme concentration and movement within the peat profile as it can limit substrate diffusion, thus affecting soil enzyme kinetics (Bonnett *et al*., 2017).

If the SOM does not reach the catotelm and subsequently stored in a recalcitrant form, it is degraded within the acrotelm to more simple molecules by plant roots exudates/microbes leading to the formation of CO_2, CH_4, and/or DOC (Worrall *et al*., 2017). Saturated anoxic soil conditions below the water table limit activity of the enzyme phenol oxidase which prevents decomposition of OM through what is termed the 'enzymatic latch mechanism' (Fenner and Freeman, 2011). Phenol oxidases are enzymes which break down recalcitrant phenolic compounds which are major carbon sinks within peatlands because of anaerobic conditions induced by a high-water table depth. In the presence of phenol oxidase, biodegradative hydrolase enzyme activity is suppressed. Aeration of the peat column increases phenol oxidase activity, thus releasing this otherwise recalcitrant carbon as CO_2. *Sphagnum* moss also releases a phenolic compound known as *Sphagnum* acid (Section 2.5.1.1) which prevents decomposition in-part via this mechanism. A reduction in phenolics concentration increases the activity of hydrolyse enzymes responsible for peat decomposition (Freeman *et al*., 2001a), thus destabilising the peatland C store.

OM decomposition in peatlands occurs at slower rates in comparison with other ecosystems as it is constrained by oxygen availability (Blodau, 2002). As a result of slow transport processes in saturated peat, decomposition products accumulate and cause a decline in decomposition rate as OM quality and availability decreases (Heinemeyer *et al*., 2010; Limpens *et al*., 2008). Plant tissues with higher lignin, polyphenol, and waxy components, and higher lignin:N and C:N ratios are more recalcitrant and therefore undergo decomposition at slower rates than those with higher polysaccharide and carbohydrate concentrations (Kleber, 2010). Primary recalcitrance influences intrinsic molecular characteristics which affects plant OM turnover times, whilst secondary recalcitrance can refer to the resistance to microbial synthesis and humification processes (Kleber, 2010).

Pathways of C loss from peatlands include gaseous and waterborne fluxes and biomass removal (Bonn *et al*., 2014). C is lost to fluvial systems via DOC and POC (Evans and Warburton, 2010), with losses from the most eroded UK blanket bog catchments exceeding ~100 g C m^{-2} yr^{-1} (Evans and Warburton, 2007). DOC is a major concern for utility companies as it causes a decline in WQ, while POC can reduce water resource by causing sedimentation in reservoirs, reducing water storage capacity (Evans and Warburton, 2010).

2.2.3 Peatland Gaseous Fluxes

Northern peatlands are a significant component of CH_4 and CO_2 terrestrial fluxes and exhibit a dual role in the radiative forcing of GHG on the environment (Frolking *et al*., 2006). Whilst both CO_2 and CH_4 are released from respiration and decomposition processes, CO_2 is also uptaken by vegetation via photosynthesis. Gaseous exchange between blanket bogs and the atmosphere is dominated by the fixation of CO_2 via photosynthesis by vegetation (Worrall *et al*., 2011a) which lowers the atmospheric GHG burden of CO_2 exhibiting a negative radiative forcing of climate (i.e., a net C sink and there exhibits a cooling effect) (Frolking *et al*., 2006). CH_4 emissions, which have a GHG potency 25 times greater (over a 100-year time frame) than CO_2, counteract this C fixation and thus negative climate forcing impact from peatlands (Frolking *et al*., 2006). The balance between C sequestration and emissions is affected by climate, peatland topography, water table height, and land management strategy. However, there is particularly large uncertainty about net CH_4 emissions from peatlands (Laine *et al*., 2007). Net CH_4 emissions can be high from very wet areas such as ditches particularly under warmer conditions (MacDonald *et al*., 1998a) and in relation to aerenchymous vegetation such as sedges via plant-mediated transfer (PMT) of CH_4 (Bhullar *et al*., 2013)..

2.2.3.1 Carbon dioxide (CO_2)

CO_2 production arises from aerobic OM decomposition (mineralisation) and plant respiration (Blodau, 2002). It is an end-product of both aerobic and to a much lesser extent anaerobic OM decomposition following the transformation of plant biomass C, POC, DOC, and microbial biomass C (Kayranli *et al*., 2010). CO_2 gaseous fluxes are a function of seasonality, location, nutrient status, and habitat status and positively correlate with temperature and oxygen levels, increasing under drained conditions (Bridgham and Richardson, 1992 and Kayranli *et al*., 2010).

The net difference between the absorption of atmosphere CO_2 and CO_2 production is known as the net ecosystem exchange (NEE) (Laine *et al*., 2006). This gaseous exchange represents a significant portion of the peatland C budget (Clay *et al*., 2010b)) and is controlled by photosynthetic active radiation (PAR) levels (Limpens *et al*., 2008), peatland hydrological regime and N and P availability (Blodau, 2002). In what may be considered 'active' status peatland, NEE is negative, meaning C is being fixed (Evans and Warburton, 2010). It is generally highest in the middle of summer and lowest in the middle of winter due to changes in photosynthesising leaf surface area of vascular plants, photosynthetic photon flux density, and soil temperature, all of which are significant controls on respiration rate (Laine *et al*., 2006). Where N availability is limited, a shallower water table and higher temperatures increase NEE (Blodau, 2002).

Decomposition within a peatland ecosystem is a complex process involving both aerobic and anaerobic processes as redox conditions exert a control over CO_2 production (Kayranli *et al*., 2010). Periodic fluctuations in oxic condition can cause 'pulses' in higher mineralisation rates following a disturbance due to enhanced biomass recycling caused by redox-induced chemical breakdown (Blodau, 2002) and the activation of exo-enzymes proceeding short-term increases in O_2 exposure (Freeman *et al*., 1997a). Moreover, vegetation type not only affects NEE but also decomposition processes via litter quality. For example, whilst non-vascular species such as *Sphagnum* generally show lower NEE than vascular species, but they also decompose at a slower rate than vascular species such as *C. vulgaris* (Blodau, 2002).

2.2.3.2 Methane (CH_4)

Northern peatland CH_4 emissions are characterised by high spatial and temporal variability (MacDonald *et al*., 1998b) and vary as a function of temperature, pH, nutrient and substrate availability, vegetation, and water table height (Basiliko *et al*., 2003). In peat soils, CH_4 production is the result of anaerobic methanogenesis and the terminal step of the anaerobic mineralisation of OM where sugars are converted to CH_4 and CO_2 (Equation 3.1) and is emitted to the atmospheric directly from the soil and vegetation or is further oxidised by methanotrophs (Abdalla *et al*., 2016a). Methanogenesis is the combined result of the interaction methanogenic microorganisms, each utilising different OM groups (summarised in Equations 2.1). These pathways of the anaerobic decomposition to the formation of CH_4 are largely controlled by the quality and quantity of OM present in the peat soil (affecting the needed activation energy or energy gain – energy balance shown in Equation 2.1 A, B, and C).

Equation 2-1 Pathways of anaerobic decomposition leading to the formation of methane and activation energies (Stępniewska and Goraj, 2014).

$C_6H_{12}O_{6\,(l)} \rightarrow 3CO_{2\,(g)} + 3CH_{4\,(g)}$	(Δ= + 1795 kJ mol^{-1})	Equation 2.1 A
$CH_3COOH_{\,(s)} \rightarrow CH_{4(g)} + CO_{2\,(g)}$	(Δ= + 18 kJ mol^{-1})	Equation 2.1 B
$CO_{2\,(g)} + 4H_{2\,(g)} \rightarrow CH_{4\,(g)} + 2H_2O^{\,(l)}$	(Δ= - 253 kJ mol^{-1})	Equation 2.1 C

CH_4 peatland fluxes are more variable than CO_2 fluxes (Limpens *et al*., 2008), with high spatial variability being observed even in homogeneous research areas (Stępniewska and Goraj, 2014). High emissions are generally found in peat with high decomposition rates, local anoxia, high provision of substrates provided by roots (i.e. exudates), and rapid transport to the surface through conduits formed by vascular plant roots (Limpens *et al*., 2008). Water table height is the primary controlling factor of CH_4 fluxes (Table 2.8) as this determines the aerobic zone depth and thus the oxidising capacity of the peat (MacDonald *et al*., 1998b). However, CH_4 production can show time delays with emissions due to build up at depth before ebullition (bubbles), which is linked to changes in temperature (particularly freeze-thaw), water tables and air pressure (Baird *et al*., 2009).

Table 2.7 Methane (CH_4) fluxes from blanket bogs with high and low water tables taken from the literature.

Peatland condition	CH_4 flux	Studies undertaken	Reference
Drier bogs with persistently low water tables.	< 1 g C m^{-2} yr^{-1}	Blanket bog study site in Ontario. Vegetation of study site included shrubs, sedges, and *Sphagnum* mosses. Static chamber method used to measure CH_4 flux.	Roulet *et al* (2007)
		Blanket bog in subarctic Sweden. Standard close chamber technique used to measure CH_4 flux. Vegetation measurements done using aerial photographs. Vegetation not specified.	Christensen *et al* (2004)
Wetter bogs with higher water tables	5-8 g C m^{-2} yr^{-1}	Blanket Bog in Ireland. *Sphagnum* and vascular plants (*Calluna vulgaris, Erica tetralix, and Molinia caerulea*) present. Closed chamber method used to measure CH_4 fluxes.	Laine *et al* (2007)
Meta analysis of various peatland types	7.6 – 15.7 g C m^{-2} yr^{-1}	Analysis of 87 studies reporting methane fluxes taken from 186 sites.	Abdalla *et al* (2016b)

2.3 Ecosystem Services in UK Blanket Bogs

ES is an umbrella term to recognise the economic value gained by society because of environmental processes (Evans *et al*., 2014). There are several classifications used to define ES, with the most common being the Millennium Ecosystem Assessment, The Economics of Ecosystem and Biodiversity, and the Common Classification of Ecosystem Services (Pereira *et al*., 2017). The Millennium Ecosystem Assessment (2003) identified four categories (Table 2.3) which can be used to describe the ES delivered by functioning blanket bog.

Table 2.3 Ecosystem Services provided by blanket bogs as described by the Millennium Ecosystem Assessment (2003).

Ecosystem Service	Service provided by blanket bog	Reference
Provision	Storage of freshwater and fuel production.	Parish *et al* (2008); Ritson *et al* (2016)
Regulation and maintenance	Hydrological flow and flood regulation, climate regulation, erosion regulation, and natural hazard regulation.	Finlayson, D'Cruz and Davidson (2005), Parish *et al* (2008), Martin-Ortega *et al* (2014), Pereira *et al* (2017)
Support	Soil formation, carbon sequestration.	Ritson *et al*., (2016)
Cultural	Physical, intellectual, spiritual, and symbolic interactions with biota, landscapes and ecosystems, education, recreational activities, palaeo-environmental archives.	Finlayson, D'Cruz and Davidson (2005), Bonn *et al* (2014), Pereira *et al* (2017)

Recreation, water provisioning, and regulation of climate are arguably the most important ES provided by blanket bogs. Upland tourism and game shooting represents a significant source of income for upland communities (Holden *et al*., 2007; Van der Wal *et al*., 2011), with restrictions imposed upon upland access during the foot and mouth crisis of 2001 leading to an estimated loss of £8 billion to the UK tourism industry (Reed *et al*., 2009) . Blanket bogs are found at the headwaters of river catchments and thus are significant sources of potable water (Peacock *et al*., 2015). It is estimated that 70% of drinking water in the UK is provided from upland catchments (Van der Wal *et al*., 2011), with mixed source peaty water constituting up to 43% of this, and the directly sourced portion is estimated at 17% (Xu *et al*. 2018). 'Active' peatlands increase hydrological resource availability and regulate water quality (Holden *et al*., 2007), and are thus assumed to reduce treatment costs for utility companies. Flood prevention, water quality regulation and climate mitigation services provided by UK uplands has been valued at £60.8K km^2 yr^{-1}, £42.6K km^2 yr^{-1} and £22K km^2 yr^{-1} respectively (Morris and Camino, 2011). However, this valuation (which is calculated using methods outlined in the Millenium Ecosystems Assessment; MEA, 2005) neglected to consider peatland type and bog condition, both of which have been impacted by anthropogenic pressures and habitat management (Evans *et al*., 2014; Pereira *et al*., 2017).

Whilst ES is a useful tool when considering the benefits to society provided by blanket bogs, the usefulness of a one-dimensional ES valuation remains contested, with some arguing ecosystem function cannot be expressed in monetary terms as they exist independently of human needs (Selivanov and Hlaváčková, 2021). Some may perceive the importance of the UK uplands differently from those viewing it through the mainstream scientific lens and therefore, conflict in values may impact decision making concerning land management (Pascual *et al*., 2017). For example, for upland landowners and communities, blanket bogs offer an income source on land which is unsuitable for other uses (i.e., for agriculture), whilst governmental bodies such as DEFRA and Natural England may view the habitat as an opportunity to enhance biodiversity and climate change mitigation . In the case of blanket bog, evidence underpinning the effects of land management and climate change upon ES (particularly for anthropogenic management) is often conflicting (Brown *et al*., 2014; Heinemeyer *et al*., 2023). Whilst the associated science could be considered as relatively mature, few studies consider a range of habitat conditions, soil type, and management techniques, and are generally designed to identify a significant experimental effect (Evans *et al*., 2014). Moreover, whilst there is considerable ongoing effort to restore bogs and their functioning, surprisingly little is known about the actual long-term outcomes and consequences, particularly in relation to C cycling affecting water quality and with regards to underlying soil processes. Of concern is that currently, underpinning soil chemical processes (such as microbial OM turnover) have not been investigated in detail as a driver of observed large scale changes in ES provisioning, and specifically water quality (DOC loading and characterisation, and water colour), in relation to both climate and management. However, ES valuation is a useful tool in justifying management, restoration, and scientific investigative costs (particularly for policy makers), and therefore will be used in this thesis.

2.4 Blanket Bog Management

Land use and management are important drivers of ecosystem function and structure (Felipe-Lucia *et al*., 2020) and within the UK, blanket bogs have historically been used for forestry, livestock grazing, game bird breeding, and as a source of fuel and horticulture medium (Ward *et al*., 2007). Due to topography and soil properties (low bulk density and high proportion of OM), the use of blanket bog is limited and therefore, the management of these areas for Red Grouse shooting is a viable economic prospect. Any past land-use changes have generally been aimed at maximising the economic benefits associated with these uses, but this has often been done at the expense of the delivery of other ES, leaving most of UK blanket bogs in a degraded state (Backshall *et al*., 2001; Natural England, 2018). The consequences of the various management techniques remain contentious, but may involve a reduction in C sequestration, WQ and drinking water provisions, and biodiversity (Bonn *et al*., 2014) resulting from alterations to hydrological regime (Price *et al*., 2003) , physical peat structure (Holden *et al*., 2014; Sherwood *et al*., 2013) , and more indirectly, microbial activity (Kitson and Bell, 2020; Lehmann *et al*., 2011).

Much of the UK upland blanket peat - especially the UK Pennines – was extensively drained for agriculture during the in the 1800s and then again in the 1960s and 1970s and has recently undergone extensive restoration through ditch blocking and rewetting (Bain *et al*., 2011) . Currently livestock grazing - i.e., sheep - (Ward *et al*., 2007) and controlled burning are the most widespread management regimes, but there are concerns surrounding drainage and burning altering C fluxes, C storage and deteriorating water quality (Evans *et al*., 2014). Subsequently, mowing has more recently been explored as an alternative method of management (Heinemeyer *et al*., 2023); however, discussion within the literature is limited and warrants further investigation (Harper *et al*., 2017; Worrall *et al.*, 2011). The following section outlines the various management options and the major concerns.

2.4.1 Prescribed blanket bog burning

Controlled burning has been employed as a land management technique in the British uplands for many centuries (Vane *et al*., 2013) , with evidence suggesting anthropogenic fire regimes began in the Mesolithic period ~ 11.6-6.0K years ago (Davies *et al*., 2008) . It is widely used to prevent woodland succession, reduce the risk of wildfires, and increase natural habitat biodiversity (Alday *et al*., 2015), and is seen to be responsible for the open, treeless moorland which is now characteristic of the British uplands (Davies *et al*., 2008). On blanket bog, short burning rotations– usually between 10 and 20 years- have been traditionally used to produce a mosaic structure of heather at various growth stages to provide a habitat for red grouse (Davies *et al*., 2008; Reed *et al*., 2009). However, there are concerns surrounding the impacts of fire upon peatland hydrology, C storage, and water quality (e.g. Evans *et al*., 2014). Since the 2005 review of the Heather and Grass Burning Code for the UK government agency DEFRA, there has been extensive work undertaken to address these concerns (e.g., Clay *et al*., 2009; Worrall *et al*., 2010; Holden *et al*., 2012; Glaves *et al*., 2013; Ramchunder e*et al*., 2013; Brown and Holden, 2013).

Peatland burning, however, remains a contentious management tool (Clay *et al*., 2010), with many studies showing contrasting results on the impacts of controlled burning (Table 2.9), meaning decision making is often difficult for landowners. Prescribed burning affects regulating, provisioning, and cultural ES (Worrall *et al*., 2010), through the alteration of vegetation community composition (as it promotes *C. vulgaris* regeneration), and C-cycling (increasing recalcitrant material soil inputs in the form of charcoal (Heinemeyer *et al*., 2018a) and decreasing litter input). This in-turn affects microbial processes (Burn, 2021). Vegetation recovery post-burn largely depends upon the condition of the vegetation community as well as the burn rotation length, and fire conditions on the day of the burn (Worrall *et al*., 2010) . Therefore, general conclusions on the impact of burning on biodiversity should be treated with caution (Worrall *et al*., 2010) .

Much of the burning debate surrounds its impact on C storage as this is seen to define 'active' bog status. However, burning impacts on ecosystem C pools are complex, affecting above ground biomass through combustion (leading to alterations in plant and microbial communities) and chemical and physical soil properties (Knicker, 2007). Soil chemical characteristics are influenced by burning through a number of mechanisms: 1) organic material deposition on the soil surface (in heather dominated systems about 5-10 % is returned as charcoal; Heinemeyer *et al*., 2018); 2) heating of the soil surface induces changes in SOM chemical structure; 3) alterations in soil physical structure (on heather dominated uplands blocking pore space and increasing bulk density; Heinemeyer *et al*., 2018 and Holden *et al*., 2014); and 4) induced water repellence (due to the deposition of hydrophobic compounds; (Kelly *et al*., 2018). The persistence of these changes depends upon vegetation recovery rates, climate, hydrology, soil characteristics, climate, and topography (Kelly *et al*., 2018)

Following fire, a layer of enhanced water repellence is found on and/or below the soil surface (Knicker, 2007) and is enriched in hydrophobic OM. This hydrophobicity can reduce soil infiltration and thus wetting, increase overland flow, soil erosion, preferential flow, and nutrient losses (Jiménez-Morillo *et al*., 2017) and has significant implications for both ecosystem function and WQ. Peat hydrophobicity is controlled by the quality of SOM- largely that of the lipid fraction. In addition, 'black carbon' (i.e. charcoal) is produced during partial combustion of biomass and exhibits resistance to degradation and is assumed to be persistent in the SOM pool (Knicker, 2007). Finally, changes in soil water chemical composition have been observed on burnt plots and evidence shows fire affects flow and water mixing pathways (Clay *et al*., 2010a). Whereas wildfire can burn into the peat, controlled burning generally affects only the uppermost litter layer and/or superficial soil horizons which generally contain the highest amount of C within the soil profile (Jiménez-Morillo *et al*., 2017). Low impact burning can promote vegetative regeneration and increase plant nutrient availability (Neary *et al*., 1999) and thus may encourage the growth of vascular plants, potentially altering vegetation community structure. However, the combustion of vegetation produces polycyclic aromatic hydrocarbons (PAHs) which can have detrimental effects on ecological receptors when their concentration exceeds a certain threshold. The transfer of PAHs to drinking reservoirs occurs via streams in both dissolved forms and in association with eroding particles (Vane *et al*., 2013).

The effects of burning on water quality is currently unclear given there is conflicting evidence presented within the literature. Some studies have reported an increase in DOC in waters draining from burnt catchments (Grayson *et al*., 2012; Ramchunder *et al*., 2013; Yallop and Clutterbuck, 2009)(. Other studies observed no changes (e.g., Ward *et al* (2007))) albeit on a plot scale and at the end of a 10-year burn cycle. Worrall *et al* (2013) reported burning was associated with a reduction in DOC, however, the studied bog was very wet, and therefore, there were fewer evaporative losses unlike at other sites. What this indicates, is that the effects of burning upon DOC are site specific.

Peat carbon budgets can be significantly altered by burning with Clay *et al* (2010) reporting a significant reduction in the overall budgets of the older burnt plots when compared to more recently burnt plots. This was attributed to higher net primary productivity (NPP); due to a higher rate of net photosynthesis in younger vegetation and lower overall net ecosystem respiration as CO_2 is more readily sequestered by younger vegetation. Moreover, the reportedly shallower water tables seen on some of the burnt plots resulted in a larger saturated zone and therefore lower rates of SOM decomposition. Therefore, longer burn rotations have a greater net C sequestration potential than shorter rotations and on unburnt plots (Clay *et al*., 2010). Another important factor seems charcoal C sequestration as shown by Heinemeyer *et al*. (2018), where increased C content and bulk densities correlated positively with higher burn frequencies. However, a more recent study by Marrs *et al* (2019) has shown that all burn rotations show less peat C accumulation rates than unburnt plots; unfortunately, they did not report detailed bulk density values, nor was charcoal density assessed. Therefore, further work is warranted.

Table 2.8 Studies reporting effects of controlled burning in UK blanket bog upon C accumulation and sequestration and blanket bog hydrology.

Study	Method	Effects on carbon	Effects on hydrological regime	Key Findings /limitations	Reference
Long-term consequences of grazing and burning on northern peatland carbon dynamics	Study site located at Moor House NMR on plots on year 9 of a 10-year burn rotation and was compared to an unburnt control. Sampling of C stocks was done over three horizons: 1) organic horizon to a depth of 1 m; 2) F and H horizons; and 3) surface litter. Samples were oven dried at 105°C. CO2 and CH4 gas flux measurements were made using the calibrated static chamber approach. Gas samples were analysed using GC/MS-FID. Soil water samples were filtered using a 0.45 µm filter and analysed on a Skalar continuous flow colorimetric system with a detection limit of 0.5 mg L^{-1}.	Reduced sequestration. Increased gross gas flux.	Not investigated.	Reduced aboveground and surface peat C stocks. Increase in gross gas fluxes which was linked to changes in vegetation community structure. / Did they measure BD and consider shrinkage/expansion?	Ward *et al* (2007)
Effects of managed burning in comparison with	Study sites were in Goyt Valley within the Peak District National Park. No managed	Decrease in soil water DOC concentrations.	Deeper water tables.	Higher water table means soil water close to the surface is acting similarly to surface runoff	Worrall *et al* (2013b)

vegetation cutting on dissolved organic carbon concentrations in peat soils.	burning within the catchment within the 5 years prior to the study, but an accidental burn occurred in 2007. Plots used were a fresh cut and leave, 1-year cut and leave moss, 1-year cut and lift, a fresh burn, 1-year post burn and 5-year post burn and a control plot. Soil water samples were analysed for common water quality parameters,	Surface runoff DOC concentrations do not differ between treatments and controls. Soil water DOC decreased significantly explained by changes in water table and flow-path.		and is mixed with rainwater which has a low DOC concentration. Decrease in depth to water table is likely due to a change in evapotranspiration due to loss of vegetation. As this was a space-for-time study, this may have differed prior to the study and be unrelated to management.	
Effects of burning and grazing on carbon sequestration in a Pennine blanket bog, UK	Study side was situated on Moor House NMR. Three different burning treatments (10 year and 20 year burning rotations and unburnt). Subsamples were dried at 105°C. Spheroidal carbonaceous particles were used as a dating tool.	After 30 years, C sequestration decreased significantly in all burnt plots regardless of rotation length.		Burning may contribute to anthropogenic C emissions through 1) decreasing peat accumulation rates; 2) inhibiting peat accumulation; and/or 3) reducing C stored within surface peat during burning. Reduction in C accumulation in burning treatments amounts to 72 g m^{-2} yr^{-1}. Abandoning this traditional management practice may provide an opportunity to increase blanket bog C storage. But spherical, carbonaceous particle dating, charcoal, and bulk density assessment questionable.	Garnett *et al* (2000)

The effects of burning and sheep-grazing on water table depth and soil water quality in an upland peat.	Study site was situated on Hard Hill within Moor House NNR. Plots had burning cycles of 10 and 20 years or no burning. Soil water samples were taken through dip-wells. Water samples were analysed for common water quality parameters.	Burning was a significant control on the pH and conductivity of soil water. Soil water DOC showed a significant decrease in the presence of burning which could not be explained by depth to water table.	Higher water tables were present on burnt plots- burning cycle frequency was not a significant factor.	Soil water DOC concentrations are influenced by time of year sampled and only a small proportion of variance is attributed to burning management. Burning has a greater impact upon depth to water table than grazing. Specific absorbance of DOC is only weakly associated with land management practice.	Worrall *et al* (2007)
Effects of moorland burning on the ecohydrology of river basins. Key findings from the EMBER project.	Focussed on ten river catchments near Ladybower Reservoir and Moor House NNR. Unburnt sites had not been burnt for >30-50 years. Other sites ranged from <1 to 25 years post burn. Soil water collected using dipwells. Peat cores were taken. Analysis of common water quality parameters was undertaken.	Burning reduces OM content of upper peat layer leaving it less able to retain exchangeable cations.	Depth to water table was significantly deeper in burnt catchments vs unburnt catchments. Hydrological properties of peat following a burn leaves the peat less conducive to *Sphagnum* growth.	Burnt sites had significant lower SOM in the surface peat and no recovery since burning appears to have occurred. Lower water tables were found on more recently burnt plots. Less overland flow in more recently burnt plots. Burning results in a reduction in soil hydraulic conductivity. Burnt sites located further east and at lower elevations than the unburnt sites, and therefore received less rainfall meaning	Brown *et al* (2014)

				deeper water tables than in the west and therefore unrelated to management. Space for Time study should have included site factors as random factors in the statistical tests.	
Effects of fire on the hydrology, biogeochemistry and ecology of peatland river systems.	Review paper.	Burning increases downstream DOC concentrations.	Burning increases depth to water table and variability in water table depth. However, some small-scale studies indicate shallower water tables on some plots.	Some studies found burning is detrimental to *Sphagnum* whilst other smaller scale studies contradict this. Near-surface peat has higher bulk density on more recently burnt plots due to decreased hydraulic conductivity and macropore flow. The effect of managed burning upon water table depth is contested, but this review is critical of smaller scale plot studies as the managed burns in these cases are extremely controlled and not representative of typical managed burns. Increase water colour in leachates from more recently burnt plots. Did not accurately consider pseudo replication in studies.	Brown *et al* (2015)

Compositional changes in soil water and runoff water following managed burning on a UK upland blanket bog.	Study site was at Moorhouse NNR. Soil water sampling initially include unburnt, 20-year burn rotation, grazed, and ungrazed plots. Samples were analysed for major cations and anions.		Less mixing between water in upper and lower layers of the peat soil column. Post-burn soil water is less mixed with rainwater.		Clay *et al* (2010a)

2.4.2 Blanket Bog Mowing

Blanket bog mowing has been proposed as an alternative to prescribed burning as it is safer (no fire risk) and retains biomass (in the form of cut heather – henceforth referred to as brash) which under the correct conditions could lead to additional peat formation. The effects of mowing upon ES delivery compared to burning are less understood and its impacts upon C cycling in peatlands is not as extensively discussed within the scientific literature compared to its counterpart (see examples in Table 2.10). More recently, a review was undertaken on behalf of Natural England which reviewed literature on the effects of cutting vegetation as a management technique (Moody and Holden, 2023). Moody and Holden (2023) stated that where mowing was considered as an alternative management regime, it was not compared to a true 'unmanaged' control and therefore, drawing conclusions to *nil*-management as a strategy is not possible. Cutting promotes vegetation (i.e. *C. vulgaris*) regeneration (Gardner *et al*., 1993a) however unlike with burning, mowing poses no direct risk of destroying soil and litter C stocks (Worrall *et al*., 2011b) . Cut vegetation left on site may act as mulch, reducing soil erosion and helping to maintain soil saturation (Worrall *et al*., 2011b), however, peat soils are at risk of compaction due to heavy machinery (Heinemeyer *et al*., 2019). Mowing typically has a higher cost compared to burning, but some of this cost can be offset through the commercial sale of heather cuttings (Backshall *et al*., 2001). In addition, mowing is not constrained by weather conditions in the same way as burning, but is made more difficult by wet, soft ground (MacDonald, 1996). The use of mowing however is limited by topography and some sites may be inaccessible to machinery (e.g., on steep slopes or in very boggy/rocky areas). In comparison to burning where vegetation is removed, brash prevents soil moisture loss through evaporation, and erosion risks posed by the removal of vegetation are also limited (Worrall *et al*., 2013b) . Brash represents a nutrient input into nutrient-poor soil and decomposing cut vegetation releases gaseous C; on large scales this can alter peatland C-budgets (Heinemeyer *et al*., 2023) . Whilst the long-term effects of mowing management on peatland C dynamics and water quality are not well understood, concerns are centred around the risk to peat soil integrity and structure. Compaction may reduce micro-topography by removing the top of hummocks, and may lead to an increase in bulk density and thus reduce water storage and peat depth (Heinemeyer *et al*., 2019) .However, higher water tables and soil moisture have been reported under mowing compared to burnt areas (Heinemeyer *et al*., 2019; Worrall *et al*., 2013b) which is likely due to the death of *Calluna*, reducing evapotranspiration and limiting root growth.

As with burning, cutting promotes vegetation (i.e. heather) regeneration (Gardner *et al*., 1993b). If cuttings (i.e., brash) are left on the bog surface, there are no immediate C losses, but this is likely to undergo decomposition contributing to gaseous C fluxes (Heinemeyer *et al*., 2018b). Unlike burning, there is no direct risk of destroying soil and litter C stocks (Worrall *et al*., 2011a). Decomposition rates in the surface (0-5 cm) were higher on mown plots where brash had been left (Heinemeyer *et al*., 2018b). Cut vegetation left on site may act as mulch, reducing soil erosion and can maintain soil saturation (Worrall *et al*., 2011a) but simultaneously, vegetation regeneration may be impeded (Heinemeyer *et al*., 2018b). The risk of wildfire may be reduced if cuttings are removed from site (i.e., fuel load), which is a likely issue on drier sites (i.e., on wetter sites, brash will remain moist).

Mowing is likely to have an impact on water quality in peatland soils, although currently this is not well understood. If vegetation cuttings are left, DOC concentrations may increase due to decomposition of the cut vegetation. However, Worrall *et al*., (2013) reported a decline in DOC, but attributed this difference to changes in water table depth and flow paths through the soil profile. Shallower water tables have been reported under burnt and mown plots, attributed to reduced water loss via evapotranspiration (Heinemyer *et al*., 2019; Worrall, Rowson and Dixon, 2013). However, long-term, it may decrease depth to water table by inhibiting the growth of deep *C. vulgaris* roots. Alterations in hydrological regime through management such as burning and mowing, which leads to higher water tables and higher soil moisture (Heinemeyer *et al*., 2023) are likely to be reflected in both water quality, and/or C gaseous fluxes, but again, this is not well understood.

Table 2.9 Studies reporting the effects of mowing on key peatland ecosystem processes reported within the literature.

Study	Method	Effects on carbon	Effects on hydrological regime	Key Findings	Reference
The effect of mowing as a restoration technique upon hydrology and water chemistry in two rich fen plant communities.	Water samples were collected using piezometers across a two-year period. Samples were filtered using a 0.45 µm pore size filter. Inorganic ions were analysed by ion chromatography. Specific ultraviolet absorbance (SUVA) was calculated at 254 nm wavelength and E2:E3 (250 nm:365 nm) ratio. Organic matter and moisture content were estimated using the loss on ignition method.	Mowing triggers prolonged nutrient release from brash leading to an increase in pH and base cations. Increased DOC release due to increase in pH due to a positive correlation with organic matter solubility.	Higher water table depths on mown plots.	No treatment effects on SUVA. Treatment effects were greatest one year following the cutting and either reduced in magnitude or were lost entirely in the second year. Litter decomposition is the main source of dissolved organic carbon and nitrogen.	Menichino *et al* (2018)
Assessing soil compaction and micro-topography impacts of heather mowing vs burning management.	Peat depth, bulk density, and peat surface micro-topography. Compared pre-management measurements/plot-level data for uncut plots with burnt and mown managed plots.	Water quality parameters were not measured.	No long-lasting impact on soil bulk density or peat depth. Micro-topography was reduced by mowing by approximately 2 cm.	Cutting may be a suitable alternative to burning on grouse moors. Compaction is likely to be site specific. Any observed bulk density changes are likely due to changes in peat moisture.	Heinemeyer *et al* (2019)

Effects of managed burning in comparison with vegetation cutting on dissolved organic carbon concentrations in peat soils.	Compared DOC concentration, water table depth, conductivity, and pH in mown and burnt plots with 'pristine' *Calluna* strands.	Significant decrease in porewater DOC concentrations in burnt and mown plots due to differences in water table depth and changes in soil water flow paths.	Decrease in depth to water table in burnt and mown sites due to reduced evapotranspiration.	Differences in DOC are due to changes in the dominant source of water within the peat profile. Cutting and burning may represent a management intervention which could be effective at reversing current DOC transfers in peat catchments.	Worrall *et al* (2013)

2.5 Blanket bog Restoration

As a result of historical degradation, blanket bogs are being prioritised for protection and restoration under EU legislation (the Habitats Directive, 92/43/EEC), with a focus on vegetation and associated biodiversity recovery (Wilson *et al*., 2011a). 'Active' peatlands deliver ES and thus the broader aim of restoration projects is to return the ecosystem to a less degraded or pristine state (Bonnett *et al*., 2017) . However, exactly what this is, is not well defined. There are several mechanisms by which blanket bog may undergo degradation which include (not limited to): drainage, afforestation, peat cutting, mismanagement (i.e., burning at too high a temperature and/or at too high a frequency), and over-grazing. The mechanism of degradation can affect key blanket bog ecosystem processes differently (Table 2.4) and therefore, the optimal restoration method depends upon degradation and peatland characteristics. Blanket bog restoration projects began with simple management strategies such as grazing prohibition and have evolved into programmes which are tailored to individual blanket bog conditions and variability (Parry *et al*., 2014). Methods include drain blocking, gully blocking, reprofiling, and bare peat stabilisation. Due to increased funding from stakeholders, projects now aim to deliver on multiple benefits including reduced erosion and carbon decomposition, thus increasing carbon sequestration (Parry *et al*., 2014).

Table 2.10 Mechanism of blanket bog degradation and subsequent effects of water quality, carbon sequestration, and gaseous emissions, and vegetation community structure as reported within the literature.

Mechanism of degradation	Effects	Example Studies
Drainage	Lowering of the water table depth. Increased DOC concentration and flux in rivers. When coupled with burning, bulk density increases. Increased soil respiration.	Holden *et al* (2004) Peacock *et al*., (2018) Sherwood *et al*., (2013)
Afforestation	Lowering of water table depth. Alteration in the composition of the phenolic soil component which can affect decomposition processes.	Chapman *et al* (2020) (Mason *et al* (2009)
Peat cutting	Decline in peat depth. Alteration to hydrological regime and soil biodiversity.	(Zarzycki *et al* (2022); Räsänen *et al* (2023); Frolking *et al* (2011)

Peatland degradation – which is typically due to drainage – results in lower water tables (Holden *et al*., 2011) which leads to peat surface subsidence (Price *et al*., 2003), increased gaseous CO_2 losses, and increased concentrations of DOC in peatland waters (Strack *et al*., 2008). Subsequently, peatland restoration generally aims to raise water table levels and restore a desirable vegetation community composition to reverse increased C (namely CO_2) fluxes and C loading in draining waters (Peacock *et al*., 2015).Effective restoration of blanket bog depends upon both above- and below-ground C cycling which is linked by vegetation-microbial interactions (Gaffney *et al*., 2018). For example, maintaining a high *Sphagnum* coverage is considered desirable for blanket bog regeneration as it increases soil wetness, lowers pH, and reduces soil water tension, thus ameliorating its own environment (Price *et al*., 2003). Restoring C-cycling processes can protect peat C stocks and re-establish peat formation process and thus carbon sequestration, maximising peatland ecosystem services (Gaffney *et al*., 2018). As C-cycling processes are reflected in pore- and surface-water chemistry, it may be possible to determine peatland restoration success upon chemical parameters determined through the investigation of- and later comparison to- 'intact' blanket bog water chemistry. However, there is no consideration of this in the current literature (to the authors knowledge).

Unfortunately, the impacts of peatland restoration on ES remain poorly understood (Wilson *et al*., 2011, Wilson, and Johnstone, 2011) . Long-term monitoring of peatlands following restoration is essential for the development of effective restoration methods, but generally periods of restoration and subsequent monitoring are only short-term (~10 years) and neglect to ensure progression to fully functional peatland (Gorham and Rochefort, 2003). Gaffney *et al* (2018) highlight that progress in restoration (i.e., towards intact conditions for water table depth, vegetation, microbial activity, and nutrient cycling) has been measured 10 years post-restoration and commonly, none of the measured parameters recover during this period and thus, peatland recovery is a slow and likely multi-decadal process.

Optimal restoration method is dependent upon mechanism of degradation and site-specific conditions (Price *et al*., 2003) and blanket bog response to restoration is reported as variable within the literature. Ditch blocking is a proposed restoration strategy to resolve the issue of widespread increases in DOC concentrations and fluxes from northern peatlands (Gibson *et al*., 2009). Approximately one-quarter of UK blanket bog has been drained via ditches (Parry *et al*., 2014) and 6% of blanket bog in England have recently been infilled or dammed (JNCC, 2011). It has been shown to reduce C export (Gibson *et al*., 2009), however this finding is not consistent across the literature. Other restoration methods including planting *Sphagnum* (via *Sphagnum* plugs) and deforestation of areas which previously underwent afforestation.

There are reports within the literature on the effects of restoration upon ES delivery (summarised in Table 2.11), however these impacts remain poorly understood (Wilson *et al*., 2011). Rewetting has been reported to lead to a decrease in DOC and particulate organic carbon (POC) in waters draining from peatland catchments along with a decrease in water colouration (absorbance at 400 nm (UV_{400} abs); Parry *et al*., 2014)). However, there have been contradictory reports stating that DOC becomes more humified following rewetting which increases water colour but is preferable in the context of water treatment (Section 2.7). Draining water was found to have low E4/E6 ratios (ratio of UV_{465} and UV_{665} absorbance) indicating that drain blocking modifies DOC composition with darker coloured humic substances becoming more dominant compared to within the intact site (Wallage *et al*., 2006). A higher DOC concentration may also be observed following rewetting due to flushing of the soil (Fenner and Freeman, 2011). Decomposition and DOC production is restricted by a high-water table whereby activity of hydrolase enzyme is suppressed. Upon drainage, this inhibitory mechanism is no longer in place, but it is not known or well understood how this recovers following rewetting (Armstrong *et al*., 2010; Freeman *et al*., 2001b).

Table 2.11 Principles of blanket bog restoration techniques and effects upon peatland carbon and hydrological regime as reported within the literature.

Restoration technique	Principles	Effect on carbon chemistry	Effect on hydrology	Reference
Rewetting via drain blocking	Placement of dams (made of peat, heather bales, plastic piling or wooden dams) along drains to raise water table depth.	Decrease in DOC and POC. Decrease in water colouration (Abs^{400}). DOC is more humified .	Decrease in stream peak flow. Generally, leads to shallower water table depth.	Parry *et al* (2014) Armstrong *et al* (2010) Worrall *et al* (2007)
Gully blocking and reprofiling	Damming gullies from the headward portion downwards to trap sediment, raise water tables and slow flow.			Parry *et al* (2014)
Bare peat stabilisation	Re-establishing vegetation using plug plants. Initially provide a temporary cover with heather brash or geotextiles and microhabitat to allow vegetation to re-establish.	Establishment of *Calluna* reduces POC export.	Decrease in stream peak flow .	Parry *et al* (2014) Rosenburgh (2015)

Long-term monitoring of peatlands following restoration is essential for the development of effective restoration methods, but generally periods of restoration and subsequent monitoring are only short-term and neglect to ensure progression to fully functional peatland (Gorham and Rochefort, 2003). Gaffney *et al* (2018) highlight that progress in restoration (i.e., towards intact conditions for water table depth, vegetation, microbial activity, and nutrient cycling) has been measured 10 years post-restoration and commonly, none of the measured parameters recover during this period. Therefore, peatland recovery is a slow and likely multi-decadal process (Price *et al*., 2003). In addition, no standard management practice can be suggested for the restoration of blanket bog generally, given that each site presents unique challenges, and the same restoration technique does not achieve the same outcome in all blanket bogs (Price *et al*., 2003). What is not well understood, is the timescale on which a recovery trajectory occurs and whether this trajectory is reflected in porewater quality.

2.6 Blanket bog and climate change

Climate change is defined by The Intergovernmental Panel on Climate Change (IPCC) as a change in the mean and/or variability of the climate over an extended period (IPCC, 2008). Anthropogenic activity is altering the Earth's climate, ecosystems, and physical properties on a global to local scale at an unprecedented rate (Stewart *et al*., 2013) with a projected average global surface temperature increase by up to 4°C by 2100 (IPCC, 2007). Climate change impacts are expected to be more pronounced at high latitudes and altitudes than in other regions (Hoegh-Guldberg *et al*., 2018; IPCC, 2018; IPCC, 2021). Warmer temperatures, alterations in precipitation patterns (increased winter rainfall and decreased summer rainfall), and an increase in extreme weather events with longer drought periods are predicted for the UK (Jenkins *et al*., 2009; Werritty and Sugden, 2012). Coupled with biodiversity loss, climate change has the potential to destabilise Earth systems (Field *et al*., 2020) and effective land management therefore represents an opportunity to address both issues simultaneously as 'twin crises' (Cohen-Shacham *et al*., 2016). C balance within blanket bog – along with soil physicochemical properties, is largely a function of climate. Climate change is expected to alter precipitation patterns in addition to temperature, which will likely alter peatland C storage (Leifeld, Steffens, and Galego-Sala, 2012; Watts *et al*., 2015) and vegetation community structure (Limpens *et al*., 2008) through several mechanisms. Increased temperatures can increase OM decomposition rates, thus increasing the microbial production and consumption of DOC. Altered peatland water budgets – through either increased temperatures and evaporation, and/or drought- may alter DOC export independent of any changes to DOC characteristics or concentrations (Pastor *et al*., 2003), while water table position changes may alter aerobic and/or anaerobic decomposition regimes .

Table 2.12 Summary of potential climate change effects upon blanket bogs. Adapted from Natural England (2015).

Cause	Consequence	Potential impacts
Increased mean annual temperature	Prolonged growing season	Encroachment of vascular plants leading to diminished dominance of vegetation thought of as typically 'peat forming'. Bracken is likely to encroach areas of degraded peat. Warming may interact with increased nitrogen deposition and thus altering plant community composition.
Increased mean summer temperatures	Increased rates of evapotranspiration	A deeper water table may lead to changes in plant community composition. Increased in POC and DOC release following winter precipitation events.
Decreased precipitation in summer months	Drought Lower soil moisture Deeper water tables	A higher drought frequency may lead to changes in plant community composition. Increased aeration of the soil column potentially leading to increased decomposition and soil C gaseous emissions. Drying of the soil may lead to increased soil erosion. Increased incidence of wildfires.
Increased precipitation in winters	Increased surface run-off	Increased runoff which may lead to increased river POC and DOC loading. Increased soil erosion.
Increased incidence of storm events	Higher incidence of intense rainfall events	Increased formation of gullies. Increased soil erosion.

2.6.1 Climatic warming

Soil C decomposition rates are a function of OM quality and temperature, and even a small temperature increase may lead to large C releases from soils (Conant *et al*., 2008) . Kinetic theory states that the temperature sensitivity of decomposition correlates with OM complexity and thus recalcitrance (Bol *et al*., 2003; Conant *et al*., 2008; Hilasvuori *et al*., 2013) . As microbial processes remove the more readily decomposable (i.e., more labile) OM from the soil C pool, decomposition rates of the remaining OM decreases with a subsequent increased temperature sensitivity of the remaining C (Hilasvuori *et al*., 2013) . Much of the data regarding the dependence of temperature upon C decomposition products is based on short-term monitoring experiments and many of the models assume the soil C pool is composed of OM with uniform temperature sensitivity (Conant *et al*., 2008) . Notably, few studies look at different peat depth (layers) responses. The rate at which C mineralisation increases with temperature is greater than is generally predicted by models, meaning any climatic warming has the potential to destabilise C soil stores (Bol *et al*., 2003; Hartley and Ineson, 2008). Peatland C export is tightly coupled with both temperature and hydrological regime. A mesocosm warming experiment by Pastor *et al* (2003) found that hydrologic DOC export is controlled by peatland water balance, contrasting with results from Freeman *et al* (2001) showing DOC export has increased alongside warming despite no change in hydrological discharge. Disentangling the effects of both upon peatland C processes is difficult, however mesocosm experiments may offer an opportunity to investigate this further.

2.6.2 Drought

Water table depth is considered the most significant regulator of wetland biogeochemistry (Ellis *et al*., 2009) and lower water tables induced by periods of drought represent a threat to C sequestration in peat soils (Ritson *et al*., 2017). Oxidase enzymes responsible for peat decomposition are enhanced in the presence of oxygen (Ellis *et al*., 2009) and following water table drawdown, DOC release and methane (CH_4) fluxes are suppressed, leading to an increase in CO_2 fluxes. This therefore reduces C sequestration within the peat column (Freeman *et al*., 1997b). The 'enzymatic latch mechanism' proposed by Freeman *et al* (2001) suggests that the oxygen limitation on a single enzyme in peatland soils may be preventing the release of a major carbon store, and subsequently has serious implications for future climate warming. Drought can stimulate bacterial growth leading to the decomposition of OM, thus increasing gaseous emission but also poses a threat during re-wetting where C atmospheric losses are increased due to drought-induced increases in soil nutrients and labile C (Fenner and Freeman, 2011b).

As drought affects OM utilisation by soil biota, it can alter the potable water treatment requirements of the DOC, and thus disinfectant by-product formation potential (DBPFP) in drinking water. During periods of drought, there may be an increase in hydrophilic DOC concentrations in surface waters (Scott *et al*., 1998) and long-term alterations to enzymatic activity due a deeper acrotelm which has been shown to affect DOC characteristics and concentrations over long periods (Fenner and Freeman, 2011b) . This can alter coagulant and flocculant demand (Edzwald, 1993) and OM removal efficiencies. However, there have been few studies which have investigated disinfectant by-product formation potential (DBPFP) during and following drought conditions in peatlands, and this warrants further study.

In higher latitudes where blanket bog forms, drought conditions are expected to increase in both frequency and duration (Watts *et al*., 2015) . Drought can alter vegetation community structure, leading to a shift from a *Sphagnum* dominated structure to an abundance of more drought-tolerant species (Ritson *et al*., 2017) . An increase in air temperature due to climate warming may lead to an increased frequency of droughts and thus lowering of the water table and destabilising enzymatic latch mechanisms (Freeman *et al*., 2001b) . A larger aerobic acrotelm may lead to increased plant litter decomposition (Evans and Warburton, 2010) which has been shown to lead to increased DOC and particulate organic carbon (POC) export to fluvial systems and increased CH_4 (Kuder and Kruge, 2001) and CO_2 atmospheric flux.

2.7 The dissolved organic carbon black box- implications for water treatment

Dissolved naturally occurring organics are ubiquitous in freshwaters (Peacock *et al*., 2014) and are a particularly prevalent concern for water companies (those responsible for the treatment and supply of drinking and waste- water for domestic and commercial use) operating in peatland draining catchments (Ritson *et al*., 2016). In addition to acting as a substrate for microbial growth, they give water an unpleasant odour, colour, and taste, and thus their removal is a key process in the production of potable water (Ritson *et al*., 2017). In recent times, an increase in DOC concentration within catchments and drinking water sources has become prevalent in the UK (Evans *et al*., 2005) and around Europe (i.e., Camino-Serrano *et al*., 2016). This has been attributed to several mechanisms: i) increased enzymatic activity induced by drought (Freeman *et al*., 2001b; Roulet and Moore, 2006), ii) increased average temperature leading to increased decomposition rates (Keller *et al*., 2004), and iii) recovery from extensive atmospheric sulphur deposition and an accompanying increase in pH (Clark *et al*., 2005) as a result of intense industrialisation in the 19th and 20th centuries (Stoddard *et al*., 2007). Fluctuations in concentration and composition of DOC within drinking water affects coagulation demand, treatment time, disinfectant type, and dose, and DBP formation (Ritson *et al*., 2014) and thus requires constant and expensive monitoring. Whilst monitoring is effective in determining efficient treatment processes, little is understood regarding the implications of compound groups on coagulant demand and DBP.

Currently, there is limited understanding of the effects of blanket bog management and restoration on peat soil porewater chemistry, and subsequently drinking water treatment (DWT) and DBP formation. It has been reported that DOC load impacts DWT by affecting coagulant demand and subsequent disinfectant dose, residual disinfectant requirements, and the formation of DBPs (Rodriguez & Rodes, 2001). Therefore, as vegetation is understood to be the dominant source of DOC within peatland ecosystems (Palmer *et al*., 2001; Tipping *et al*., 2010; Grayson *et al*., 2012), processes which alter vegetation coverage are hypothesised to impact DBPFP and DOC treatability.

Rotational burning management for promoting *C. vulgaris* coverage (Noble *et al*., 2018) can lead to a seasonal addition of labile organic matter (OM) due to lower litter recalcitrance (Ritson *et al*., 2016). The dominance of vascular plants (especially aging heather *versus* managed heather, either cut or burnt), over *Sphagnum* also leads to a decline in surface horizon soil moisture. This leads to a deeper water table depth (Heinemeyer *et al*., 2023; Worrall *et al*., 2013) thus increasing decomposition (Kim *et al*., 2021), leading to waters with DOC heavily characterised by large, recalcitrant, hydrophobic compounds due to preferential utilisation of more simple compounds (Biester *et al*., 2014). Previous work by Ritson *et al* (2016) found that vascular plant derived DOC was removed from water less efficiently compared to DOC derived from *Sphagnum,* so peatlands dominated by vascular vegetation may prove more problematic for DWT. However, this study used standing dead biomass of vascular plants rather than analysing *in situ* porewater from areas dominated by such vegetation. As to date, no work has investigated peat pore water for DOC treatability, removal, and DBP formation on porewaters from peatlands undergoing various management regimes.

Peatland restoration (e.g., drain blocking) generally aims to raise water tables, which reduces the zone within the peat soil column by which enhanced decomposition and heterotrophic soil respiration occurs (Ma *et al*., 2022). Whilst there has been some work (for example Martin-Ortega *et al*., 2014) on the impacts of restoration upon water quality (WQ) more broadly (i.e., DOC loads and colour), there has been little research on whether restoration is beneficial to WQ in the context of DOC treatability. Similarly with blanket bog management, there is a wealth of work discussing the impacts of management upon WQ and C cycling, but limited work dedicated to investigating the production of DBPs and the ease of DOC removal from peatland-draining waters under different management regimes.

In addition to restoration and management practices, a change in climate can affect water table depth and thus a range of peatland processes (Holden *et al*., 2011) along with a shift in plant phenology (Antala *et al*., 2022). Studies have widely reported an increase in DOC export from peatlands with projected temperature increases, meaning DBP precursor load and thus DBPs are projected to increase (Valdivia-Garcia *et al*., 2019). A modelling study predicted a 39% increase in THM production in WTWs by 2050 under a 1.8°C mean temperature increase and showed significant correlations between THM formation and temperature (Valdivia-Garcia *et al*., 2019). Subsequently understanding if and how management and restoration can be utilised to reduce both DFP formation and DFPBP of raw waters is vital for more sustainable water treatment practices moving forwards.

In recent years, there has been a lot of work to characterise and quantify the reactivity of OM in source waters to effectively predict and manage DBP formation following chlorination (Ates *et al*., 2007; Padhi *et al*., 2019). Surrogate parameters such as UV absorbance indices – mostly $SUVA_{254}$ – are used due to correlations between DOC concentrations and the formation of THMs (Singer & Chang, 1989; Valdivia-Garcia *et al*., 2019). This is because aromatic sites substituted with oxygen- and nitrogen- containing groups constitute the sites attacked by chlorine during chlorination, thus affecting absorbance in the UV range (Ates *et al*., 2007; Edzwald *et al*., 1985). However, the usefulness of SUVA (UV absorbance corrected for DOC concentration) as an indicator of OM reactivity has been questioned, as it does not capture the reactive sites on OM moieties responsible for DBP formation in low-SUVA waters (Ates *et al*., 2007; Roccaro & Vagliasindi, 2009; Weishaar *et al*., 2003). SUVA has also been used to predict the percentage removal of OM following coagulation (Marais *et al*., 2019) and has been reported to be affected by overlying vegetation community composition (Peacock *et al*., 2014).

2.7.1 Drinking Water Treatment

Traditional water treatment approaches have focussed on in-house treatment with effective coagulant and filtration processes. However, due to increased DOC loading in source waters, water treatment works are facing operational difficulties (Sharp *et al*., 2006) and thus, to limit the chemical demand of raw waters and the associated costs, water companies are starting to adopt a more holistic approach focussing on 'treatment at source' rather than at 'end of pipe'. The role of catchment-scale processes and land management upon water quality is therefore now a key focus in catchment management, such as that pursued by Yorkshire Water Services and United Utilities in Northern England.

Water treatment usually involves coagulation-flocculation to remove DOC (thus reducing colour and improving taste), followed by disinfection -most commonly with free chlorine or chloroamine- to reduce microbial load (Figure 2.7). Whilst the disadvantage of coagulation is its cost, chlorination may result in the formation of trihalomethanes, carcinogenic disinfection by-products (DBP) whose concentrations in drinking water are heavily regulated (Peacock *et al*., 2018), and thus penalties for exceeding regulatory guidelines are substantial (Brooks *et al*., 2015).

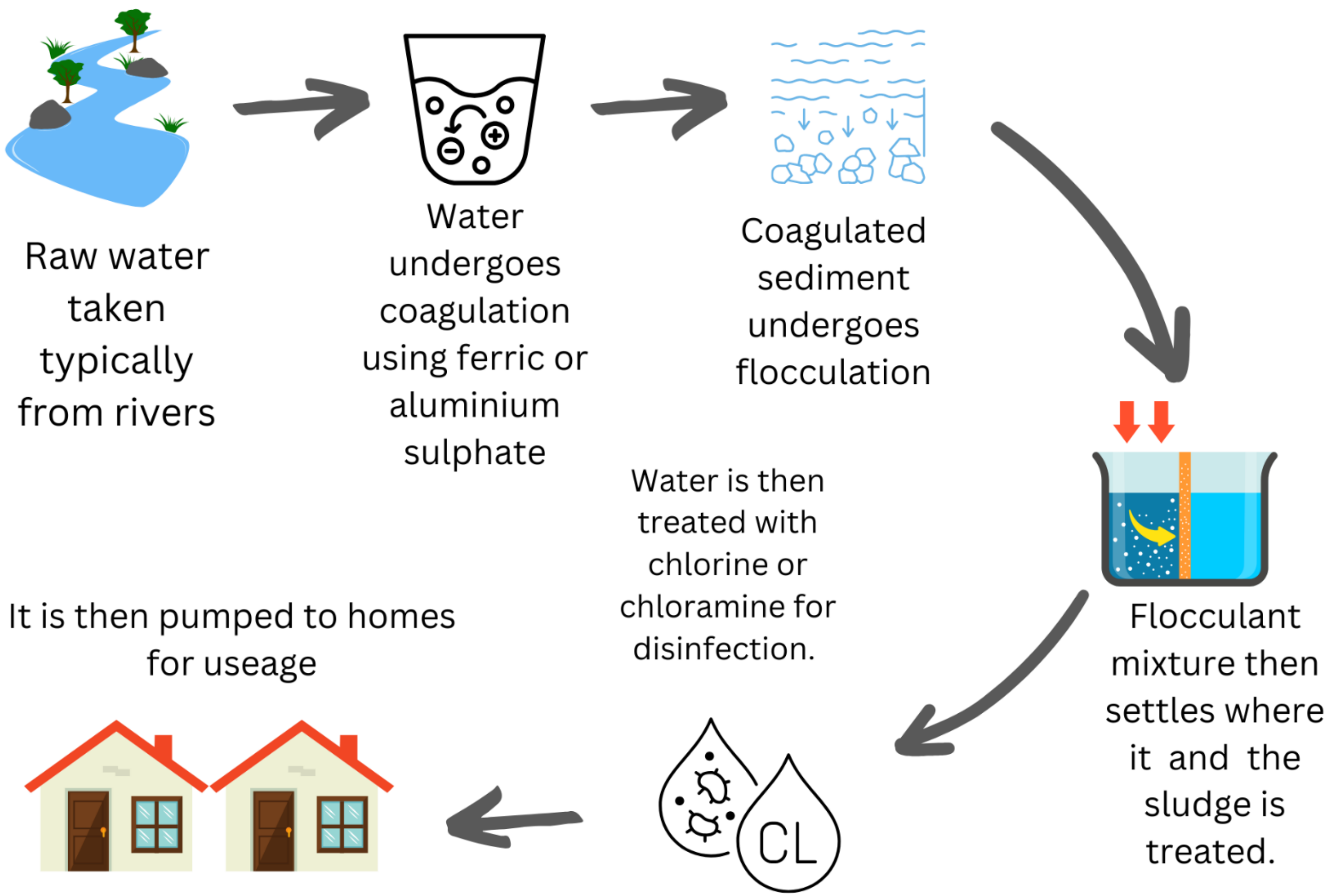


Figure 2.8 Schematic of the drinking water treatment process typical within water treatment works in the UK.

2.7.1.1 Removal of DOC from drinking water

The removal of DOC from raw water is usually the first step in the drinking water treatment (DWT) process and can be achieved through physical and chemical processes (Sadrnourmohamadi and Gorczyca, 2015). Current options include membrane filtration, ion exchange/adsorption, ozonation/biodegradation, and coagulation (Bond *et al.*, 2010; Edzwald, 1993). Negative charges and the chemical structure of hydrophobic acids affect chemical reactions with coagulants, particularly with metal-based coagulants. The removal of natural organic matter (NOM) can involve hydrolysis, complexation, precipitation, and adsorption reactions (Edzwald, 1993). Coagulants are pH dependent and show varied results with changes in raw water characteristics. The hydrolysis products of Al-based coagulants and Fe-based coagulants have positive charges which promote the formation of flocculants through charged neutralisation or sweep flocculation (Nawaz *et al.*, 2014) which can then be easily removed from waters. It is important to note that hydrophobic and hydrophilic DOC require different removal processes, with hydrophilic compounds being more troublesome during water treatment due to an affinity to remain in solution.

2.7.1.1.1 Coagulation

Coagulation is the process by which suspended particles in water are consolidated into a larger colloid which can then be flocculated and removed from the water. Coagulants can either be organic or inorganic in nature, but inorganic coagulants are most used in the UK. These include aluminium (e.g., aluminium sulphate, aluminium chloride, and sodium aluminate) and iron (ferric sulfate, ferrous sulphate, ferric chloride, and ferric chloride sulphate) coagulants. These conventional coagulants are generally more effective at removing higher molecular weight, hydrophobic compounds- particularly hydrophobic organic acids. The hydrophobic fraction of DOC contains aromatic, carboxyl, carbonyl, and long-chain aliphatics, whilst the hydrophilic fraction is made up of carbohydrates, amino acids and sugars, peptides, and proteins (Sadrnourmohamadi and Gorczyca, 2015). The most effective coagulants don't necessarily remove the most DOC, but those groups with the greatest potential to form DBPs due to a high degree of aromaticity.

Coagulation mechanisms include charge complexation/precipitation for soluble compounds and charge neutralisation for colloidal material (Sharp *et al.*, 2006), whereby hydrated inorganic hydroxides form producing short polymer chains which enhance micro- and heavy-floc formation. Optimal coagulant rates occur under acidic conditions between the iso-electric point of the coagulant and the NOM, which is pH 4.4-5.5 for ferric-based and pH 5-6 for aluminium-based coagulants. The decrease in pH from neutral pH causes functional groups to become less negatively charged due to protonation, requiring less coagulant to achieve neutralisation (Sadrnourmohamadi and Gorczyca, 2015). They are also effective at removing a significant portion of DBP precursors (see Section 2.7 and 2.8) and have a low unit cost. Disadvantages of inorganic coagulants is that they produce metal-rich flocculant, and their disposal adhere to strict environmental standards, thus increasing treatment costs. Aluminium based coagulants are widely used and effectively remove much of the DOC at a relatively low cost. Polymeric aluminium coagulants are becoming more widely used and are more effective in the removal of turbidity and TOC and the reduction of UV_{254} under some concentrations. The effectiveness of chemical coagulants depends largely upon characteristics of the raw water (Sadrnourmohamadi and Gorczyca, 2015).

There is an indication that vascular plant-derived DOC is less readily removed during coagulation-flocculation treatment, whilst compounds associated with *Sphagnum* mosses are more likely to undergo microbial mineralisation prior to reaching treatment plants (Ritson *et al*., 2016). Lower molecular weight, aliphatic compounds more readily undergo mineralisation prior to treatment than higher molecular weight, aromatic compounds. Humic compounds are more easily removed from drinking water than proteinaceous compounds (Ritson *et al*., 2016). In waters with generally high DOC loading or seasonal peaks, coagulant demand during treatment is increased, leading to an increase in disinfectant demand and sludge production (Ritson *et al*., 2016).

2.7.1.1.2 Chlorination

Since the 19th century, drinking water disinfection processes have been central to preventing the spread of pathogens, and can be considered one of the most significant advances in the protection of public health. Chlorine and its derivatives are widely used as disinfection agents due to a relatively low cost and high oxidative capacity. However, if OM remains in the water, DBPs can form, which are carcinogenic and thus heavily regulated against (Benítez *et al*., 2021).

2.7.1.2 Disinfection by products (DBPs)

DBPs are formed during reactions between precursor materials (DOC) (Bond *et al*., 2012) and disinfectants during drinking water treatment, many of which are detrimental to human health (Bond, 2009). In excess of 500 DBPs have been identified (Malliarou *et al*., 2005) and are now ubiquitous in drinking water supplies (Yang *et al*., 2019) causing concern that long-term consumption of waters containing even low or trace levels of DBPs may lead to an increase in cases of cancers and birth defects (Yang *et al*., 2019) . However, whilst all DBPs are a cause for concern, only trihalomethane (THMs) are routinely monitored in the UK. Unlike THMs- which have a regulatory limit of 100 µg L^{-1} - there are currently no limits for haloacetic acids (HAAs), and little is known regarding the presence and behaviour of HAAs in drinking water (Malliarou *et al*., 2005).

DBPs are formed during disinfection processes using chlorine, chloramines, ozone, CO_2, and UV. However much of the attention has been directed towards chlorinated DPBs given that chlorine is the most widespread disinfectant (Bond, 2009). On a mass basis, THMs and haloacetic acids are thought of as the dominant DBPs within drinking water (Bond, 2009) with haloacetronitriles, haloketones, haloacetaldehydes, and halonitromethanes being less of a concern but nonetheless important (Bougeard, 2009) (Figure 2.8).

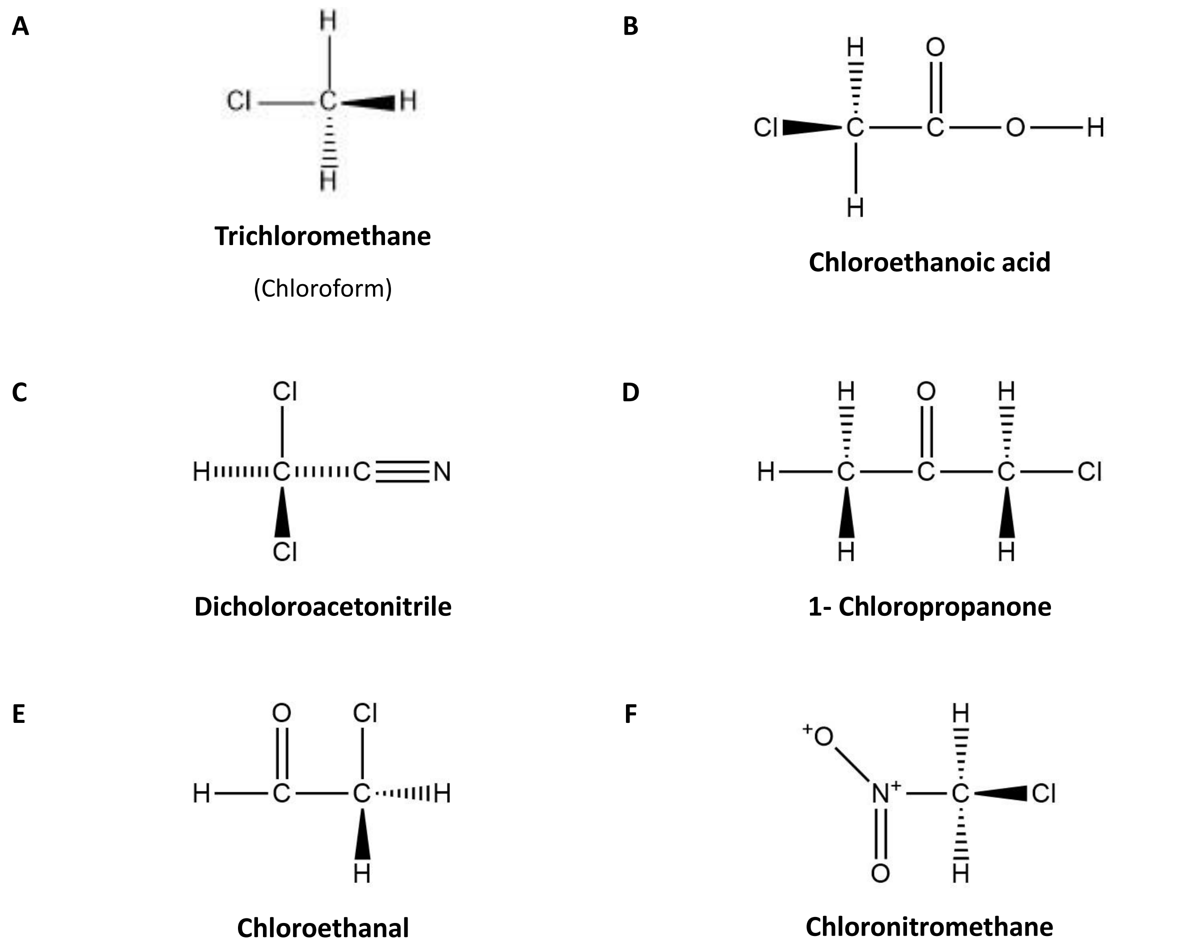


Figure 2.9 Disinfection by-products commonly found in drinking water- Examples of a: trihalomethane (A); haloacetic acid (B); haloacetronitrile (C); haloketone (D); haloacetaldehydes (E); and a halonitromethane (F).

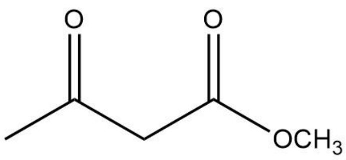
DBPs can be controlled through catchment management, precursor treatment, disinfection, and removal post-treatment. Catchment management is particularly attractive to water treatment companies, given it is a preventative method rather than a cure for the issue. DOC in water from any catchment is heterogeneous in nature and this is reflected in the diversity in DBPs (Parsons *et al*., 2009). In the case of blanket bog, knowledge of DBP precursor nature and subsequent transformation during transportation down the peat column and from peatland to reservoir is currently largely unknown.

2.7.1.3 Disinfection by-product precursors

Whilst the treatability of DOC within drinking water can be predicted in terms of physicochemical properties, DBP formation cannot be predicted in the same way (Bond *et al*., 2010). Currently surprisingly little is known regarding the precursors for the formation of DBPs (Yorkshire Water, per comms, 2019). Generally hydrophobic DOC – that is humic and fulvic acids, and other organic macromolecules rich in phenolics and conjugated double bonds - is a more significant source of DBPs precursors, whilst hydrophilic DOC- aliphatic carbon and nitrogenous compounds is seen to be less significant but still contains a significant level of precursors (Table 2.13) (Bond *et al*., 2010; Hua and Reckhow, 2007). Several aliphatic β-diketones and β-diketoacids (Figure 2.9) have high THM and HAA formation potential (Parsons *et al*., 2009) . Hydrophilic OM fractions are less amenable to treatment by coagulation than the hydrophobic fraction, and therefore where chlorination is the final treatment step, it is largely hydrophilic moieties which determine DBP formation (Parsons *et al*., 2009; Bond *et al*., 2010). A study by Owen *et al* (1993) found that the hydrophilic fraction exerts a greater chlorine demand compared to the hydrophobic fraction (2.4 mg Cl_2 mg^{-1} DOC and 0.32 mg Cl mg^{-1} DOC respectively), and thus had a higher THM formation potential.

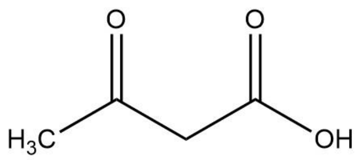
Table 2.13 Trihalomethane (THM) formation potential per mg DOC for the major groups of dissolved organic carbon in drinking water. Legal upper limit for drinking water is 100 µg L^{-1}.

Chemical group	Nature	THM potential (µg THM mg^{-1} DOC)	Reference
Humic acids	Hydrophobic	46	Parsons *et al* (2009)
Fulvic acids	Hydrophobic	27	



Pentane-2,4-dione

β-diketone



3-Oxobutanoic acid

β-diketoacids

Figure 2.10 Examples of β-diketones and β-diketoacids- aliphatic compounds with high trihalomethane and haloacetic acid forming potentials.

Traditionally, water treatment has focussed on the removal of turbidity and thus colour, however as DBPs became a greater concern, treatment is increasingly becoming optimised for the removal of DOC (Parsons *et al*., 2009). DBP formation studies largely use model compounds to act as surrogates for the main chemical groups found in DOC, and therefore the classification of DBP forming compounds rarely extends to the molecular level (Bond *et al*., 2010).

2.7.2 Detection of DBP precursors in drinking water

The presence and level of DBP precursors in drinking water can be detected directly (using techniques such as GC-MS and NMR which are destructive, relatively costly and time consuming), or using inference methods (such as UV absorbance which are non-destructive, fast, and comparatively low in cost).

UV absorbance (UV_{abs}) in both the characterisation of OM in natural waters and the disinfectant byproduct formation potential (DBPFP) of a water is a useful tool as absorbance has been linked to hydrophobicity, molecular weight (Edzwald *et al*., 1985) and the aromaticity of DOM (Weishaar *et al*., 2003a). As hydrophobic and hydrophilic compounds absorb different wavelengths, UV absorbance could be used as a proxy for DBPFP. Absorbance at 254 nm (UV_{254}) is widely used to characterise WQ in peatland draining catchments, as aromatic compounds are the dominant component of OM in such waters and absorb light at this wavelength (Peacock *et al*., 2014). However, it is not suitable for all waters, as some DBP precursors do not absorb within this region (e.g.., hydrophilic compounds including simple sugars) (Weishaar *et al*., 2003a).

Differential measurements (e.g. changes in UV absorbance prior to and following chlorination) may be a more useful tool in the prediction of the DBPFP of a water. Changes in absorbance at 272 nm (UV_{272}) 2 hours post-chlorination (-Δ272 nm, t = 2h) has been suggested to be a useful predictor of chlorine reactivity (Roccaro and Vagliasindi, 2009). However, reaction times for some OM groups are longer than this and so may significant underestimate DBPFP. This has not been widely investigated and therefore warrants further study.

2.7.3 DBP formation in peatland draining waters

To date, there has been little work on the impact of various peatland management techniques and restoration practices upon the DBPFP of peatland waters. There has been work however into the potential impacts of climate change upon DBP formation from peatland draining catchments (Valdivia-Garcia *et al*., 2019) and the potential of various peatland vegetation types to be significant producers of DBP precursors (Ritson *et al*., 2016).

DOC loading of peatland-draining waters has increased due to climate change (Ferretto *et al*., 2021a; Freeman *et al*., 2004; Lee *et al*., 2020; Salimi & Scholz, 2021; Xu *et al*., 2020a) and habitat degradation (Bussell *et al*., 2010), which has been linked to vegetation management (Clutterbuck & Yallop, 2010; Grayson *et al*., 2012). However, there has not been sufficient work into understanding the links between management and restoration practices and the disinfectant by-product formation potential (DBPFP) of peatland draining waters.

In peatland ecosystems, vegetation is the dominant DOC source (Palmer *et al*., 2001; Tipping *et al*., 2010; Grayson *et al*., 2012), and therefore processes which alter vegetation coverage are hypothesised to impact DBPFP and DOC treatability. Rotational burning and mowing management may lead to an increase in *C. vulgaris* coverage with an associated seasonal additional of labile OM (Ritson *et al*., 2016). Vascular plant dominance may lead to a deeper water table (Heinemeyer *et al*., 2023; Worrall *et al*., 2013) which increases decomposition with the soil column (Kim *et al*., 2021). Potentially, this could lead to waters being increasingly characterised by large, recalcitrant, hydrophobic compounds due to preferential utilisation of more simple compounds (Biester *et al*., 2014). Key vegetation types (i.e., *Calluna*, *Sphagnum* and *Molinia*) have been shown to have different DBPFP. Vascular plants exhibit higher above-ground biomass production compared to *Sphagnum* and thus represent a seasonal soil input of labile OM with a lower recalcitrance. Whilst such compounds are more readily broken down by soil biota, they prove problematic to DWT as they are less amenable to removal by coagulation and flocculation (Ritson *et al*., 2016). Therefore, trajectory towards *Sphagnum* dominated vegetation community composition may be more desirable. Whilst there is a wealth of work discussing the impacts of management upon water quality and C cycling, there is very limited work dedicated to investigating the DBP production and DOC removal efficiency from peatland-draining waters under different management regimes.

In additional to vegetation management practices, climate change may alter a range of peatland processes (Holden *et al*., 2011)(along with changes in plant phenology (Antala *et al*., 2022). With projected temperature increases, DBP precursor (DOC) concentrations are expected to increase in peatland draining waters. This is accompanied by a predicted 39 % increase in THM production in water treatment works by 2050 under a 1.8°C mean temperature increase (Valdivia-Garcia *et al*., 2019). Subsequently understanding if and how management and restoration can be utilised to reduce both DFP formation and DFPBP of raw waters is vital for more sustainable future water treatment practices under increasing climate pressures.

2.8 Review of Methodologies

2.8.1 Mesocosms in peatland studies

Mesocosms are becoming increasingly prominent in ecological studies and are a useful experimental tool, allowing a bridge between more tightly controlled experiments (which may not be representative of real-world conditions) and the great complexity of natural systems (Stewart *et al*., 2013). Environmental conditions can be controlled (in this context examples include water table depth and temperature), allowing rigorous study of ecological responses to perturbations without the need for repeated extensive fieldwork expeditions. They are central to understanding and predicting the impacts of climate and climate change upon ecological systems and ecosystem processes at different levels (i.e., species – communities) (Fordham, 2015). Whilst not a perfect experimental set-up, mesocosms can be used to overcome economic and time challenges associated with carrying out robust field experiments.

In peatland studies, cores of peat soil are commonly taken and experientially manipulated. Typically, mesocosms are not buried (i.e., Laine, Strömmer and Arvola, 2014; Mulot *et al*., 2015), however, this leaves them exposed to wider temperature fluctuations which would not be typical of *in situ* conditions. Therefore, maintaining as-close-to field conditions is important in obtaining meaningful results. In the study of ombrotrophic bog, there is the additional challenge of maintaining a water table depth representative of that measured in the field with water from a low-mineral and nutrient source (i.e., rainwater and/or deionised water).

2.8.2 Analytical approaches used in the characterisation of organic matter in peatland studies

The investigation and characterisation of SOM is often a cumbersome process due to its diverse nature as a result of different parent vegetative material, dispositional conditions, and subsequent transformative processes (Bu *et al*., 2019). The analytical methods commonly used in the study of peatland SOM are: 1) ultraviolet-visible (UV) absorbance; 2) mass spectrometry (MS); 3) infra-red spectroscopy (IC); and 4) liquid chromatography (LC) These techniques each reveal different aspects of molecular structure: e.g., C environment, molecular weight, concentration, and functional groups, and therefore, a combination of these techniques is often applied in SOM characterisation (Grandy and Neff, 2008).

Each of the methods described have both advantages and disadvantages, and often interpretation of the ascertained spectra is difficult. The complexity of both soil and analytical processes makes the investigation and understanding of C biogeochemical processes in peat soils difficult (Grandy and Neff, 2008) and therefore it is important to utilise several methods to verify results. The analysis of peatland SOM is important to further the understanding of how land management impacts soil C cycling processes to maximum ES, thus improving WQ and contributing to the mitigation of climatic warming.

2.8.3 UV Spectroscopy use in characterising organic matter composition

Ultraviolet-visible absorbance spectroscopy (UV-vis) is a relatively simple method used to quantify DOC in natural waters (Peacock *et al*., 2014). UV-vis spectra arise due to a transition in electronic energy levels, whereby an electron in a low-energy orbital state is promoted to a higher energy orbital. The absorbance wavelength corresponds to the difference in energy (*E*) between the concerned orbitals (Williams and Flemming, 2008) and is a function of a molecular structure and concentration (Weishaar *et al*., 2003b) . Whilst it cannot provide specific information regarding individual molecules within a sample, UV-vis spectra can indicate specific bonding arrangements within OM (Weishaar *et al*., 2003b) . However, UV can only be used to identify functional groups which are UV-absorbing (Table 2.15) however given that the humic fraction-which comprises the majority of DOC in natural water samples- absorbs light in the UV range of the electromagnetic spectrum, it is useful to alluding to OM composition (Peacock *et al*., 2014).

UV absorbance can be used as an indication of DOC aromaticity and thus reactivity (Peacock *et al*., 2014). Given that the aromaticity of DOC determines its reactivity with disinfectants in the water treatment process, it is an important parameter for reactivity with coagulants and thus may be used to indicate DBP formation potential (Weishaar *et al*., 2003). Other wavelengths are also used as proxies for DOC concentration: for example, the E_2:E_3 index is used as a molecular weight proxy and E_2:E_4 indicates OM humification (Ritson *et al*., 2016) (Table 2.15). Absorbance at 254 nm is commonly employed by the water industry as a measure of DOC, given that the UV absorbing fractions of OM are main contributors to DBP formation (Marais *et al*., 2019).

Table 2.14 UV-vis parameters used in the investigation and characterisation of DOC. Adapted from Peacock *et al* (2014).

Proxy	Wavelength (nm)	Comment	Reference
E_2:E_3	250:365	Ratio correlates with molecular size and aromaticity of aquatic humic matter. Increased E_2:E_3 indicates increased aromaticity and decreased molecular size.	Peuravuori and Pihlaja, (1997)
E_2:E_4	252:452	252 nm is used as a proxy for DOC concentration. 252:452 is gives an indication of DOC composition. Represents the intensity of UV-absorbing functional groups compared to those giving the water its characteristic brown colour. A greater concentration of humic substances will yield lower 252:452 values.	(Graham *et al* (2012)
	254:436	Absorbance at 254 nm provides an estimation of concentration and can characterise the origin and properties of DOC in whole-water samples.	(Selberg *et al.*, (2011)
E_4:E_6	400:600	Gives a general indication of the nature of DOC. High 400:600 ratio suggests a dominance by low molecular weight organic compounds or fulvic acids.	(Moore (1987)
	450:650	Provides a measure of fulvic:humic substances which contribute to water colour and relative peat humification.	(Wilson *et al.*, (2011a)
	465:665	Used as an indicator for humification (degree of organic matter decomposition). Decreasing E_4:E_6 ratios indicates progressive humification. Not applicable for use in limnology.	Peuravuori and Pihlaja, (1997)
SUVA	254	$SUVA_{254}$ for natural waters is generally 0.6-6 L mg^{-1} C m^{-1}. It is positively correlated with aromatic C present in DOC. Represents microbial vs terrestrial ($SUVA_{254}$ < 3 L mg^{-1} C m^{-1} vs > 4 L mg^{-1} C m^{-1} respectively). Values are correlated with coagulation performance during treatment whereby as $SUVA_{254}$ increases, DOC removal increases.	Comstock *et al* (2010)
	280	This wavelength may not represent the maximum absorbance for all aromatic DOC components but was used as π->π* electron transition occurs ca. 270-280 nm for phenolic arenes, benzoic acids and PAHs with $\geqslant$2 rings.	(Peuravuori and Pihlaja, (1997) (1997)
	400	Comparison of DOC with colour (specific absorbance) allowed for the composition of DOC responsible for water colour to be investigated and to be compared between treatments.	(Worrall *et al.*, (2007)

2.8.3.1 *Specific UV absorbance and the characterisation of organic matter composition*

Specific UV absorbance (SUVA) is the UV absorbance at a given wavelength per mass of DOC (Worrall *et al*., 2007) and represents the 'average' absorptivity for all molecules comprising DOC in a sample (Bougeard, 2009; Weishaar *et al*., 2003b). It is commonly used as a surrogate measurement by the water industry (Chow *et al*., 2003) for DOC hydrophobicity or hydrophilicity (Table 2.16) (Parsons *et al*., 2009). It is an indicator of the reactivity of aquatic humic compounds present in a sample and is defined as the UV absorbance at 254 cm^{-1} divided by DOC concentration (mg L^{-1}) (Weishaar *et al*., 2003a) .

Table 2.15 Typical $SUVA_{254}$ values and organic matter characteristics in waters (Edwald and Tobiason, 1999)

$SUVA_{254}$ (L m-mg C)	Characteristics of organic matter in water source
> 4	Aquatic humic substances High hydrophobicity High molecular weight
2 - 4	Aquatic humic substances and other organic matter Mixture of hydrophobic and hydrophilic substances Intermediate molecular weight
< 2	Non-humic substances Low concentration of hydrophobic compounds Low molecular weight

$SUVA_{254}$ can provide an indication of DBP formation potential. Waters with higher $SUVA_{254}$ are more reactive with chlorine and are therefore treated more effectively by traditional disinfection methods (Parsons *et al*., 2009) . Ritson *et al* (2016) found $SUVA_{254}$ correlated well with DBP formation between pre- and post-coagulation samples. It is assumed that $SUVA_{254}$ is good reflection of the humic DOC fraction and subsequent coagulation treatments are effective at removing it (Weishaar *et al*., 2003a).

2.8.4 Fourier Transform Infrared Spectroscopy

FT-IR provides rapid characterisation of specific functional groups (Chapman *et al*., 2001; Heller *et al*., 2015) and can distinguish between carbohydrate, cellulose, lignin, lipids, and proteinaceous fractions in SOM. During FT-IR analysis, covalent bonds within a molecule selectively absorb radiation of specific wavelengths, altering the vibrational energy within the bonds. As different bonds and functional groups absorb different frequencies, transmittance patterns can give an indication of the functional groups and molecules within a sample. Absorption characteristics can subsequently be used to characterise and monitor temporal changes of SOM in response to factors such as land management and climate (Elliott *et al*., 2007), and when combined with multivariate statistics can be used to differentiate between soil horizons (Artz *et al*., 2006). In addition, through the analysis of bulk samples, secondary reactions and chemical artefacts associated with wet chemical extractions can be avoided (Heller *et al*., 2015) .

Whilst FT-IR is useful in broadly characterising the nature of SOM (Table 2.17), it is somewhat limited in the study of peat soils (Table 2.18). Any detailed interpretation of FT-IR spectra is complex due to the heterogeneity of peat soils which leads to overlapping of absorption bands, meaning the resultant FT-IR spectra represents the sum of all absorption bands rather than showing detailed analysis of well-defined organic components (Heller *et al*., 2015). Subsequently, it is more useful in the evaluation of peat organic matter quality and relating it to functional chemical attributes rather than providing detailed chemical characteristics (Chapman *et al*., 2001). In a 2001 study, Chapman *et al.* used FT-IR to investigate changes in SOM quality along a transect from moorland through to wetter bog and concluded that whilst FT-IR was a useful analysis in distinguishing between major vegetation zones, its prediction of peat properties was poor.

Table 2.16 Typical spectral bands of common soil organic matter chemical groups of Fourier-transform infrared spectroscopy analysis. Quoted directly from the literature.

Band (cm^{-1})	Characteristic	Reference
3500 - 3200	Hydroxyl groups in alcohols, phenols and water molecules.	(Heller *et al* (2015)
3020-2800	Stretching of aromatic C-H bonds	Naumann *et al* (1996); Celi *et al (*1997); Eliott *et al* (2007).
2920 - 2860	Stretching of aliphatic C-H bonds.	As above
1700 - 1610	Stretching of C=O bonds which are part of amides, carboxyls or carboxylic acids, carboxylates, ketones, aldehydes, and esters.	(Heller *et al* (2015)
1170-1100	C-O or C-OH groups in glycopeptides or complex carbohydrates.	Naumann *et al* (1996); Celi *et al (*1997); Eliott *et al* (2007).
1100 - 1050	Stretching vibrations of C-O-C bonds in polysaccharides such as cellulose.	(Heller *et al* (2015)

Table 2.17 Summary of examples of studies characterising peatland soil organic matter using Fourier-transform infrared spectroscopy.

Investigation aims	Sample preparation and method	Findings	Reference
Prediction of organic matter composition in peat samples at various stages of peatland restoration.	Peat cores were taken and separated into horizons. 1 cm^3 subsamples were taken and mixed to ensure homogeneity and dehydrated by freeze drying and powdered using zirconium balls. FT-IR spectra were acquired by averaging 200 scans and 4 cm^{-1} resolution over 4000-350 cm^{-1}. Carbohydrate analysis was undertaken on fine-grained peat fractions and cellulosic and hemicellulosic sugars were quantified by gas chromatography after hydrolysis.	FT-IR allowed for reconstruction of peat C:N ratio and carbohydrate signatures but not the micromorphological composition of vegetation remains. The combination of FT-IR spectra and carbohydrate (<200 µm fraction) allowed for determination of plant cell wall constituents in peat and revealed the composition of parent vegetation material. FT-IR, C:N ratios, and carbohydrate signatures were adequate in the initial screening of organic matter composition of peat.	Artz *et al* (2008)
Changes in peat organic matter composition following the expansion of native pine forest across open moorland.	Cores were taken along three parallel transects from open moorland to forest. The forest litter layer and *Sphagnum* layer were removed from the cores. Moisture content, C:N ratio, ash content, and pH were measured. Peat sub-samples were dried at 105°C and finely milled. FT-IR spectra was obtained over 4000-349 cm^{-1} in ~2 cm^{-1} intervals. Spectra data was subjected to PCA and CVA analysis.	FT-IR spectra of peat from three different vegetation zones were significantly different and showed correlation with peat physical/chemical properties. Correlation with biological parameters were less significant.	Chapman *et al* (2001)
Evaluation of organic matter composition and microbial community composition in peat horizons of varying levels of decomposition.	Peat cores were taken to 30 cm depth and split into 4 horizons determined by degree of humification. FT-IR was used to confirm differences in the degree of decomposition. FT-IR analysis was coupled with microbial assays.	Combination microbial assays and FT-IR may be a powerful technique to determine microbial influence on the cycling of labile carbon in peatlands.	Artz *et al* (2006)
Determine the relationship between peat properties and degree of humification.	1 mg of dried milled peat combined with 400 mg of KBr to produce a homogenised pellet analysed using FT-IR. Elemental analysis of C, H, N, and S, UV, and TOC	Peat diagenesis can be described with a multiproxy analysis using age, degree of decomposition, chemical and physical properties, and parent	Silamiķele *et al* (2010)

	analyses were also undertaken. Humification degree was determined using NaOH and expressed as absorption.	vegetative material. Using a multi-analysis approach a better understanding of peat properties and how they influence decomposition processes can be assessed.	

2.9 Literature review summary

This chapter has attempted to review the important literature surrounding the effects of management, restoration, and climate change upon ES delivery in UK blanket bog along with peatland water quality in the context of drinking water treatment. C-cycling in peatlands are reflected in pore- and surface-water chemistry, and therefore catchment management may offer a more sustainable alternative to traditional end-of-pipe drinking water treatment methods. In addition, the trajectory from degraded to restored blanket bog may be reflected in the water chemistry. There is no consideration of this in the published literature at the time of writing. In recent times, interest in peatland restoration has increased (Gorham and Rochefort, 2003), particularly in the UK uplands, to maximise ES provision. However, there is scientific uncertainty surrounding the effects of various upland land management practices on water provision and quality, C accumulation, and climate change mitigation (Reed *et al*., 2009) and this literature review has shown that there is conflicting evidence. This makes reaching a definitive consensus regarding best management and restoration practice difficult.

Therefore, in summary,

- The impacts of prescribed burning upon ES delivery in UK blanket bog have undergone extensive investigation, however, this has not been considered against alternative mowing and if preferential management is site specific.
- It is widely accepted that degraded UK blanket bog needs to undergo restoration, however there is no consensus of the impacts of this restoration upon ecosystem service delivery. There is currently no outlined trajectory against which is assess if restoration is successful either in vegetation community or water chemistry.
- Current understanding of the treatability of waters draining from peatlands with varying vegetation community composition is limited and therefore, the effects of management regimes, restoration practices and status, and climate upon drinking water treatment and quality is limited.

Therefore, in this work, field, mesocosm, and laboratory studies will be undertaken to assess water quality (i.e., treatability) and GHG emissions alongside management, restoration status, and climate to improve understanding of the underpinning processes as drivers of key ES.

3 Methodology

3.1 Introduction

This chapter outlines the study sites, mesocosm core collection and experimental setup within this thesis. Whilst several hypotheses were tested in this work, investigations were all undertaken within the same experimental setup. The following sections describe: the field sampling sites and rationale behind their selection (Section 3.2) mesocosm peat core design (Section 3.3.1) and core collection and the experimental set-up at the University of York's experimental site (Section 3.3.2), pore water sampling (Section 3.3.4) and analysis (Section 3.3.7), gas flux analysis (Section 3.3.8), and drinking water treatment (Section 3.7)which formed the bulk of this work.

3.2 Site selection

Ombrotrophic blanket bog sites were selected to be investigated to test the effects of management and climate upon ES delivery. Three heather-dominated blanket bog sites under grouse moor management (field sites being monitored as part of the Peatland ES-UK project (Heinemeyer *et al.*, 2018) were selected to test the effects of vegetation management. Blanket bog sites in Exmoor, Peak District and Scotland were selected to investigate the effects of habitat spectrum and peatland restoration. The combination of sites ranged from warm/dry to wet/cold to test the effects of climatic conditions. The sites forming the habitat status and peatland restoration part of this thesis were selected after consultation with local site managers and owners, and thus site selection could be viewed as a reflection of the opinion of the site managers. The terminology of 'intact' and 'degraded' blanket bog status and its meaning is ill-defined (Heinemeyer and Ashby, 2021) and so may differ depending upon the management organisation and their objectives. Notably, the 'intact' sites are likely better referred to as 'near intact' sites - as they were still under some historic management, likely negatively affecting their habitat condition and peatland functions. While the habitat status categorisation was used as a condition for site selection, some flexibility was given in meeting the key criteria – i.e., sites being restored ~8 years ago were still considered as 5-year post restoration. Restoration status was chosen to categorise samples; however, it was not known whether this spectrum of habitat condition would be reflected within the data, and this will be tested in this thesis.

In site selection we also considered financial and logistical constraints. Selected sites were those where recent management was known, and with proximity to a road or track as each mesocosm would be transported manually. Finally, each condition within each site (i.e., management and restoration status) needed to be of similar altitude to ensure climate conditions were similar.

3.2.1 Site codes and naming

Sample sites were coded based upon location and management or restoration status as well as replicate number. Examples are given in Table 3.1.

Table 3.1 Site and management/restoration codes used throughout this thesis.

Site codes:	Management codes:	Replicates
Grouse managed blanket bog (testing management regimes)		
N – Nidderdale M – Mossdale W – Whitendale	F – burnt (i.e., managed with fire) M – Mown U – Uncut/unmanaged	4
National sites (testing peatland restoration)		
S- Scotland P – The Peak District E – Exmoor	10 Y - ~10 years post restoration 5 Y - ~5 years post restoration D – Degraded I - Intact	3
Example Mossdale Uncut replicate 2 – MU2 The Peak District degraded replicate 3 – PD3		

3.2.2 Site Descriptions

For this thesis, blanket bog cores were taken at six locations spanning from the south of England to the north of Scotland (Figure 3.1) which were of varying climatic and habitat conditions and under different management regimes (Figure 3.2 and Table 3.2). Samples from two sites in Yorkshire (Nidderdale and Mossdale) and one site in Lancashire (Whitendale, Forest of Bowland) formed the heather management aspect, and three sites (Exmoor, the Peak District, and Scotland) formed the peatland restoration aspect of this work. Cores collected from all six sites were included in the analysis of the effect of climate.

Table 3.2 Study site summaries. More detailed descriptions can be found in the text (Section 3.2.3 and Section 3.2.4). All descriptions are pers comm. from site managers at Southwest Water (Exmoor), RSPB (Scotland), Moors for The Future (The Peak District) or were taken from the Peatland ES-UK report (Heinemeyer *et al*., 2019).

Site	Region	Lat – Long	Site codes	Management/Restoration status
Nidderdale	Yorkshire, England	54.16619, -1.9154346	NF, NM, NU	Grouse moor managed. Rotationally burnt and mown and unmanaged (uncut) plots.
Mossdale	Yorkshire, England	54.314726, -2.2940051	MF, MM, MU	Grouse moor managed. Rotationally burnt and mown and unmanaged (uncut) plots.
Whitendale	Yorkshire, England	53.990898, -2.5030333	WF, WM, WU	Grouse moor managed. Rotationally burnt and mown and unmanaged (uncut) plots.
Crocach	Sutherland, Scotland	58.376965, -4.0163539	SD	Degraded area of deep gripped blanket bog. Suspected previous muirburn but not since early 1990s.
The Uair	Sutherland, Scotland	58.411833, -4.0292684	S5Y	~ Five years since gully blocking for restoration (2012).
Nam Breac	Sutherland, Scotland	58.390931, -3.9936438	S10Y	~ Ten years since gully blocking for restoration (2004).
Forsinard Bog Pools	Sutherland, Scotland	58.369028, -3.9687441	SI	'Intact' area of blanket bog in the vicinity of bog pools.
Halsworthy	Exmoor, England	51.132925, -3.7561221	ED	Degraded blanket bog. Disturbed in the 19th century for mineral prospecting and drainage.
Spooners	Exmoor, England	51.121903, -3.7517172	E5Y	~ Five years since restorative gully blocking of grips which were installed in the 19th century for agricultural expansion.
Hangley Cleave	Exmoor, England	51.164599, -3.6963237	E10Y	~ Ten years since restorative gully blocking of grips which were installed in the 19th century.
Squallacombe	Exmoor, England	51.16245, -3.8102619	EI	'Intact' blanket bog which had previously been restored. Historical ditching.
Kinder Scout	The Peak District, England	53.400792, -1.8664658	PD	Extensively degraded area of bare peat. Currently a control area for a project ran by Moors for The Future.
Bleaklow (south of)	The Peak District, England	53.457536, -1.8583664	P5Y	~ Five years post restoration. Restored from bare peat in April 2012 with lime, fertiliser, and grass seed.
Kinder Scout	The Peak District, England	53.397933, -1.8656774	P10Y	~ Ten years post restoration. Restored from bare peat in April 2011 with lime, fertiliser, and grass seed.
100 m north of Snake Pass (A57 road)	The Peak District, England	53.434574, -1.8692649	PI	Hydrologically 'intact' blanket bog. Site currently used as part of The University of Manchester's 'Making Space for Water' project.

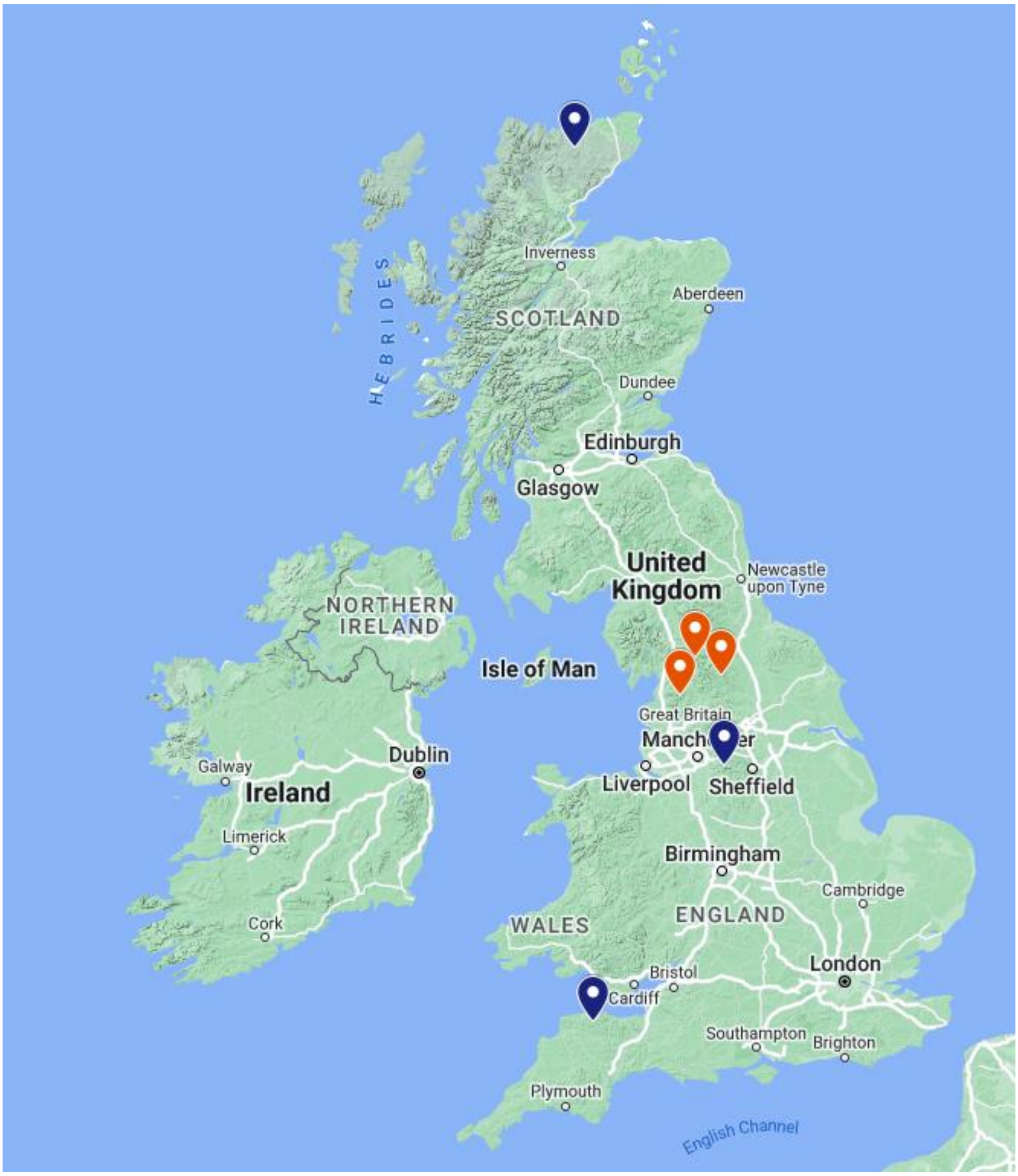


Figure 3.1 Map of the mesocosm sampling sites. Sites indicated in red are the three heather-dominated and grouse moor managed blanket bog sites (Nidderdale, Mossdale, and Whitendale) whilst the sites indicated in blue represent the sites for the degraded, -restored and near intact blanket bog sites. All sites represent a wide range of a UK blanket bog habitat and climate spectrum. Map made using Google My Maps.

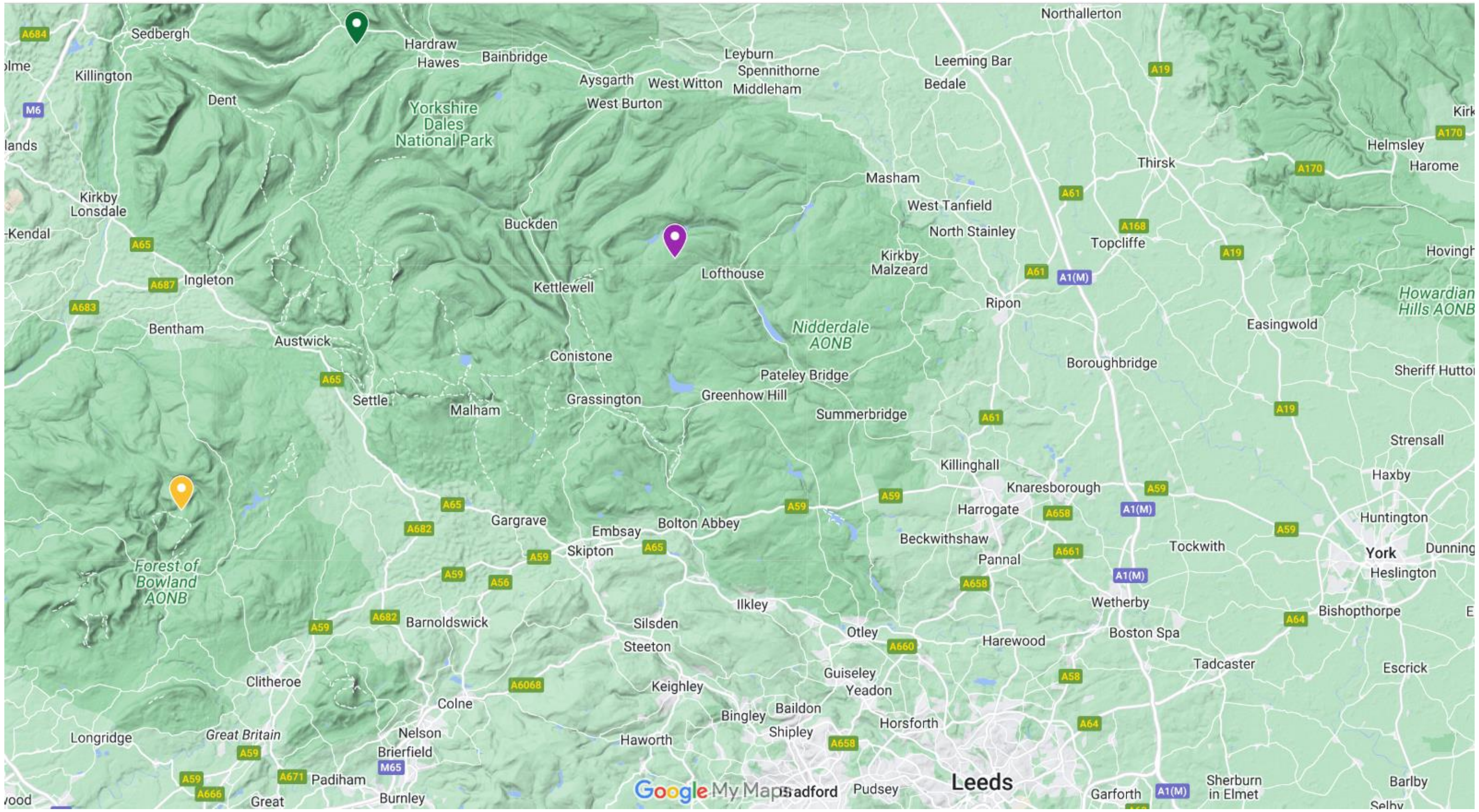


Figure 3.2 Locations of the heather-dominated and grouse-moor managed blanket bog sites. Nidderdale is shown in purple, Mossdale in green, and Whitendale in orange. Map produced in Google My Maps.

3.2.3 Vegetation management site overview

The three study sites selected for the investigation of heather (vegetation) management effects form the study sites of the Peatland ES-UK project -previously Defra funded project BD5104 (Heinemeyer, 2023). These sites are situated in north-west England and are hereby referred to as Nidderdale, Mossdale, and Whitendale. Each site constitutes two adjacent (Nidderdale and Mossdale) or close by (distance of 750 m; Whitendale) sub-catchments of around ~10 ha, each with its own stream. Following a pre-treatment period, sub-catchments underwent either a prescribed burning or mowing heather management (starting in 2013 and continuing across different areas within the catchments over time) and regular monitoring of carbon, water, and biodiversity aspects has taken place since 2012 (see Heinemeyer *et al*., 2023).

These sites were selected based on common criteria: all sites were classed as blanket bog and managed for grouse shooting with a mean peat depth of >1 m. Historically sites were managed using 10-15 year burning rotations for >100 yr (based upon initial gamekeeper and estate information; however, actual burn rotations were confirmed to be around 20 years; see Heinemeyer *et al*., 2018) with a recent low stock density of <0.5 ewes ha^{-1}. *Calluna* cover on all sites exceeded 50% and all sites had at least some existing bog vegetation (i.e., *Eriphorum* and *Sphagnum* species). All sites had comparable weather conditions and altitudes and were in proximity allowing all sites to be visited within one day.

3.2.3.1 Nidderdale

Nidderdale is situated within the Middlesmoor estate in the Nidderdale valley within the Yorkshire Dales National Park at 54°10’07”N; 1°55’02”W (UK grid reference SE055747). It is approximately 450 m above mean sea level (AMSL; m) and had a mean annual air temperature of 7.2 °C and annual precipitation of 1587 mm (2012-2021). It is situated on mudstone from the Millstone Grit group with intermingled sandstone (Kidd, Copper, and Crayson, 2007) and the soil is a poorly draining organic peat from the Winter Hill series. Manual peat rod measurements taken across the site showed peat depth ranged from 0.2 m to 2.9 m, with an average depth of 1.6 ± 0.3 m. The burnt catchment was approximately 11 ha and the mown 13 ha.

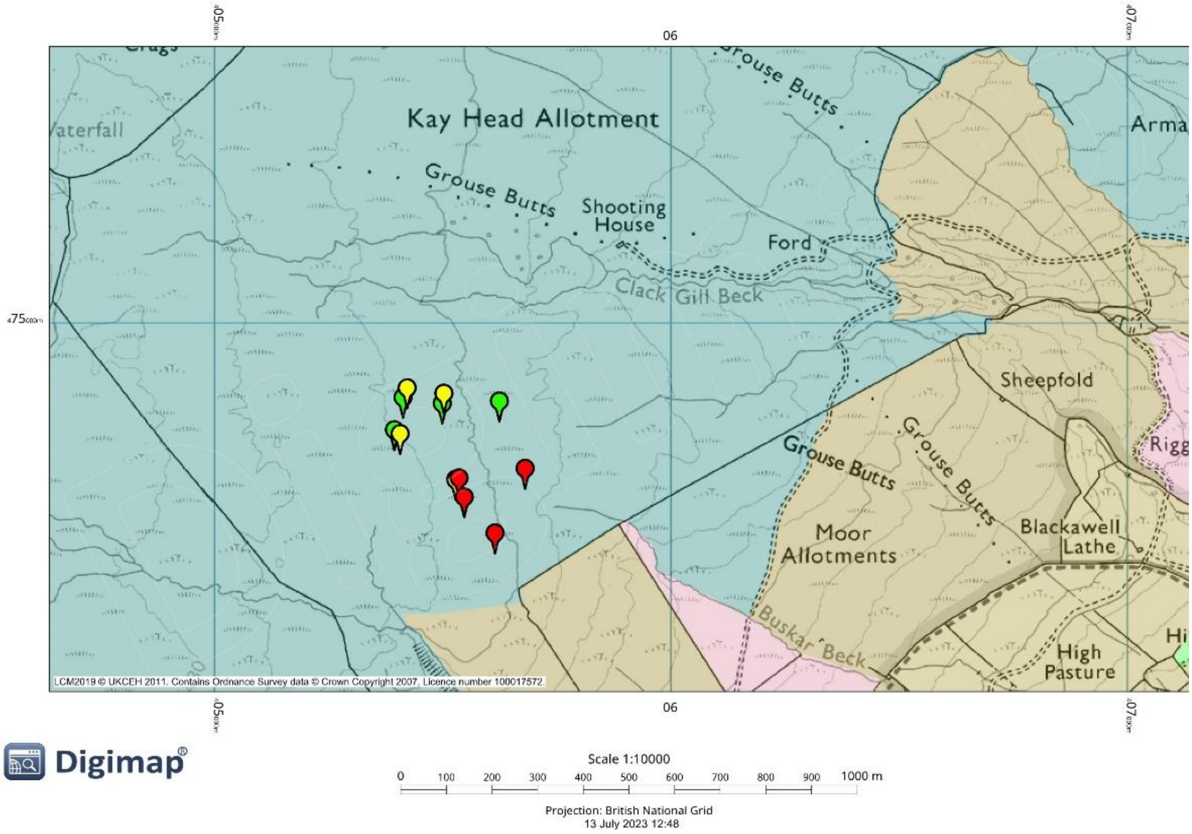


Figure 3.3 Map of the points where all heather management mesocosms were taken at Nidderdale. Red points show the burnt (F) cores, mown (M) cores are shown in green, and the adjacent uncut (U; i.e., nil heather management) cores are shown in yellow. Map produced on Digimap using landcover from 2019.

Table 3.3 Nidderdale mesocosm core site characteristics and locations. Elevation is given in meters above sea level, BNG refers to British national grid coordinates.

Management	Core	Mesocosm code	Peat depth (cm)	Slope (°)	Aspect	Elevation (AMSL; m)	BNG	Latitude	Longitude
Burnt	1	NF1	107	6	86	406	SE0561974491	54.166191	-1.9154346
	2	NF2	110	4	60	416	SE0568574630	54.167439	-1.9144212
	3	NF3	176	8	75	409	SE0555374570	54.166901	-1.9164441
	4	NF4	190	4	90	411	SE0553674609	54.167252	-1.9167037
Mown	1	NM1	235	3	60	413	SE0540074716	54.168215	-1.9187849
	2	NM2	191	10	70	413	SE0541974787	54.168853	-1.9184927
	3	NM3	228	4	100	409	SE0550574774	54.168735	-1.9171756
	4	NM4	260	6	78	443	SE0563074779	54.168779	-1.9152609
Uncut	1	NU1	197	4	50	415	SE0553674609	54.167252	-1.9167037
	2	NU2	218	3	80	451	SE0541474709	54.168152	-1.9185706
	3	NU3	150	5	85	437	SE0542874808	54.169041	-1.9183544
	4	NU4	226	4	90	438	SE0550774796	54.168933	-1.9171446

Table 3.4 Vegetation surveys and images of cores in-situ prior to core collection at Nidderdale, Yorkshire Dales. *Sphagnum* moss coverage included in moss % coverage. N refers to 'Nidderdale', F to burnt plots, M to mown plots, and U to uncut (I.e., nil heather management). % vegetation coverage was recorded only for canopy cover. Three mesocosm cores taken from each site (one large, central core and two smaller side cores).

NF1

Vegetation type	% cover
Calluna	25
Moss	65
Sedge	10
Bare	0

NF2

Vegetation type	% cover
Calluna	60
Moss	25
Sedge	15
Bare	0

NF3

Vegetation type	% cover
Calluna	30
Moss	30
Sedge	40
Bare	0

NF4

Vegetation type	% cover
Calluna	35
Moss	30
Sedge	25
Bare	10

NM1

Vegetation type	% cover
Calluna	35
Moss	20
Sedge	40
Bare	5

NM2

Vegetation type	% cover
Calluna	20
Moss	12
Sedge	68
Bare	0

Notes: 2% of moss present was *Sphagnum*.

NM3

Vegetation type	% cover
Calluna	15
Moss	20
Sedge	0
Bare	65

NM4

Vegetation type	% cover
Calluna	20
Moss	10
Sedge	0
Bare	70

NU1	NU2
	

Vegetation type	% cover
Calluna	35
Moss	40
Sedge	0
Bare	25

Vegetation type	% cover
Calluna	70
Moss	10
Sedge	0
Bare	20

NU3	NU4
	

Vegetation type	% cover
Calluna	85
Moss	10
Sedge	0
Bare	5

Vegetation type	% cover
Calluna	60
Moss	20
Sedge	0
Bare	20

3.2.3.2 Mossdale

Mossdale is situated in Upper Wensleydale within the Yorkshire Dales National Park at 54°19’01”N; 2°17’18”W (UK grid reference SD813913) It is approximately 390 m AMSL and had an average annual air temperature of 7.2 °C and annual precipitation of 2029 mm since the beginning of the project (2012-2021). The underlying geology is limestone overlain by a thin sandstone and mudstone layer, and its peat soil is poorly draining and part of the Winter Hill series. Manual peat rod measurements undertaken in 2012 showed peat depth ranged from 0.3 m – 2.1 m with a mean of 1.2 ± 0.4 m (Heinemeyer *et al.*, 2018). The burnt catchment was approximately 8 ha and the mown 10 ha.

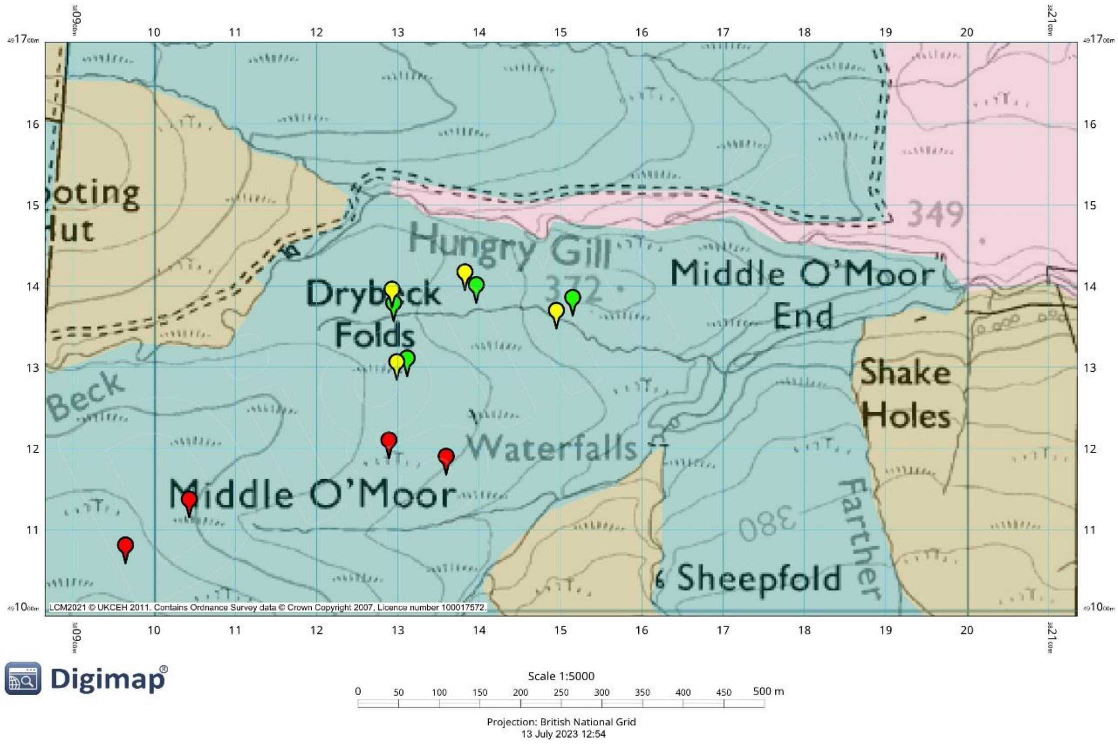


Figure 3.4 Map of mesocosm sampling locations at Mossdale, Yorkshire Dales. Red points show the burnt (fire managed, F) cores, mown (M) cores are shown in green and adjacent uncut (U) cores are shown in yellow. Map produced on Digimap with land coverage base map from 2019.

Table 3.5 Site descriptors for Mossdale, Yorkshire Dales mesocosm cores. Elevation is given in meters above sea level, BNG refers to British national grid coordinates.

Management	Core	Mesocosm code	Peat depth (cm)	Slope (°)	Aspect	Elevation (AMSL; m)	BNG	Latitude	Longitude
Burnt	1	MF1	130	14	64	402	SD8097191055	54.314726	-2.2940051
	2	MF2	100	18	80	393	SD8104891113	54.31525	-2.2928252
	3	MF3	61	16	100	389	SD8129591183	54.315889	-2.2890329
	4	MF4	74	18	110	388	SD8136491163	54.315712	-2.287971
Mown	1	MM1	120	4	88	394	SD8131691284	54.316797	-2.2887164
	2	MM2	108	2	90	382	SD8129891352	54.317408	-2.2889974
	3	MM3	138	2	90	380	SD8140191373	54.3176	-2.2874154
	4	MM4	103	2	162	378	SD8152191360	54.317488	-2.2855699
Uncut	1	MU1	100	7	70	392	SD8130691278	54.316743	-2.2888698
	2	MU2	120	7	98	383	SD8129691373	54.317596	-2.2890295
	3	MU3	60	8	70	383	SD8138791393	54.317779	-2.2876319
	4	MU4	200	3	114	372	SD8150191347	54.31737	-2.2858765

Table 3.6 Vegetation surveys and images of cores in-situ prior to Mossdale core collection. *Sphagnum* moss coverage included in moss % coverage. M refers to 'Mossdale, F to burnt plots (i.e., fire managed), M to mown plots, and U to uncut (I.e., nil heather management). % vegetation coverage was recorded only for canopy cover. Three mesocosm cores taken from each site (one large, central core and two smaller side cores).

MF1

Vegetation type	% cover
Calluna	40
Moss	15
Sedge	40
Bare	5

MF2

Vegetation type	% cover
Calluna	30
Moss	30
Sedge	40
Bare	0

MF3

Vegetation type	% cover
Calluna	5
Moss	85
Sedge	5
Bare	5

Notes: Condition noted as poor.

MF4

Vegetation type	% cover
Calluna	10
Moss	5
Sedge	80
Bare	5

Notes: Condition noted as poor.

MM1

Vegetation type	% cover
Calluna	20
Moss	75
Sedge	5
Bare	0

MM2

Vegetation type	% cover
Calluna	15
Moss	5
Sedge	80
Bare	0

MM3

Vegetation type	% cover
Calluna	30
Moss	60
Sedge	10
Bare	0

MM4

Vegetation type	% cover
Calluna	5
Moss	80
Sedge	15
Bare	0

MU1

Vegetation type	% cover
Calluna	30
Moss	25
Sedge	65
Bare	0

MU2

Vegetation type	% cover
Calluna	75
Moss	10
Sedge	15
Bare	0

MU3

Vegetation type	% cover
Calluna	40
Moss	40
Sedge	20
Bare	0

MU4

Vegetation type	% cover
Calluna	45
Moss	50
Sedge	5
Bare	0

3.2.3.3 Whitendale

Whitendale is situated within the Forest of Bowland which is recognised as an area of outstanding natural beauty in Lancashire at 53°59’04”N; 2°30’03”W (UK grid references SD672543). It is approximately 420 m AMSL and had an average air temperature of 7.6 °C and annual precipitation of 1858 mm since the beginning of the project (2012-2021). The site is underlain by interbedded sandstone and mudstone with some areas being entirely mudstone (Ewen *et al*., 2015). Manual peat rod measurements taken in 2012 showed peat depth ranged from 0.2 m – 4.5 m with an average depth of 1.7 ± 0.4 m (Heinemeyer *et al.*, 2018). The burnt catchment was approximately 8 ha and the mown 11 ha.

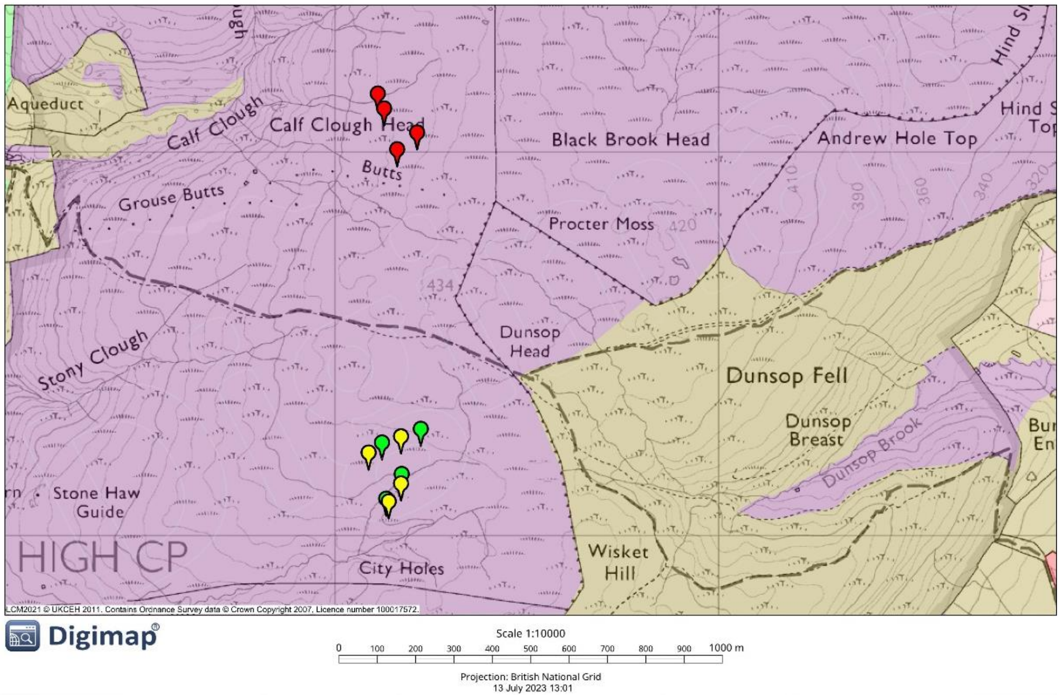


Figure 3.5 Map of mesocosm sampling locations at Whitendale, Forest of Bowland. Red points show the burnt ((F; i.e., fire managed) cores, mown (M) cores are shown in green and adjacent uncut (U; i.e., nil heather management) cores are shown in yellow. Map produced using Digimap with a base land cover (2019) map.

Table 3.7 Site descriptors for Whitendale, Forest of Bowland mesocosm cores. Elevation is given in meters above sea level, BNG refers to British national grid coordinates.

Management	Core	Mesocosm code	Peat depth (cm)	Slope (°)	Aspect	Elevation (AMSL; m)	BNG	Latitude	Longitude
Burnt	1	WF1	126	10	324	402	SD 67116 55101	53.59272	-2.30 110
	2	WF2	142	8	298	405	SD 67134 55065	53.59261	-2.30 100
	3	WF3	116	5	310	422	SD 67220 55001	53.59240	-2.30 052
	4	WF4	193	10	312	418	SD 67168 54960	53.59227	-2.30 081
Mown	1	WM1	200	7	148	419	SD 67127 54194	53.58579	-2.30 118
	2	WM2	167	7	160	414	SD 67231 54231	53.58591	-2.30 072
	3	WM3	180	5	300	411	SD 67177 54109	53.58552	-2.30 072
	4	WM4	162	7	266	410	SD 67138 54046	53.58531	-2.30 089
Uncut	1	WU1	170	6	132	423	SD 67095 54165	53.58570	-2.30 118
	2	WU2	145	9	40	410	SD 67178 54210	53.58584	-2.30 072
	3	WU3	247	5	270	414	SD 67178 54090	53.58545	-2.30 072
	4	WU4	155	7	256	407	SD 67146 54039	53.58529	-2.30 089

Table 3.8 Vegetation surveys and images of cores in-situ prior to Whitendale core collection. *Sphagnum* moss coverage included in moss % coverage. W refers to 'Whitendale', F to burnt plots, M to mown plots, and U to uncut (i.e., nil heather management). % vegetation coverage was recorded only for canopy cover. Three mesocosm cores shown (one larger central core and two smaller side cores).

WF1

Vegetation type	% cover
Calluna	10
Moss	90
Sedge	0
Bare	0

WF2

Vegetation type	% cover
Calluna	20
Moss	35
Sedge	40
Shrub	5
Bare	0

WF3

Vegetation type	% cover
Calluna	25
Moss	70
Sedge	5
Bare	0

WF4

Vegetation type	% cover
Calluna	25
Moss	60
Sedge	15
Bare	0

WM1		WM2	
			
Vegetation type	**% cover**	**Vegetation type**	**% cover**
Calluna	30	*Calluna*	0
Moss	10	Moss	40
Sedge	60	Sedge	60
Bare	0	Bare	0
WM3		**WM4**	
			
Vegetation type	**% cover**	**Vegetation type**	**% cover**
Calluna	30	*Calluna*	40
Moss	10	Moss	5
Sedge	60	Sedge	55
Bare	0	Bare	0

WU1

Vegetation type	% cover
Calluna	50
Moss	40
Sedge	10
Bare	0

WU2

Vegetation type	% cover
Calluna	45
Moss	45
Sedge	10
Bare	0

WU3

Vegetation type	% cover
Calluna	50
Moss	40
Sedge	10
Bare	0

WU4

Vegetation type	% cover
Calluna	20
Moss	10
Sedge	70
Shrub	0

3.2.4 National sites overview

3.2.4.1 Scotland

The Scottish blanket bog sampled from as part of this thesis was situated within the Forsinard Flow Country approximately 33 km south-west of Thurso. During the post-war period, the area was afforested (Sitka spruce; *Picea sitchensis*) as it was considered a viable and sensible land management option (Warren, 2000). In 1994, the area was acquired by the RSPB (Wilkie & Mayhew, 2003) where restoration projects such as tree felling and drain blocking occurred. It is difficult to ascertain a detailed management history of individual sites within Forsinard that did not undergo afforestation, but from the literature, it can be inferred that the area was widely used for shooting, grazing, and stalking with the possibility of historic muirburn management.

Although this work avoided forest-to-bog restored areas, it is still important to be considered as all sampled sites were surrounded by afforested land. The intact site, in close proximity to the Forsinard bog pools (see Figure 3.6), represents some of the most intact blanket bog in the UK. However, it is interesting that the overall peat depths in that area was low compared to deeper depths at the degraded and restored sites (Table 3.9). This site was not gripped, and subsequently has remained very wet and thus would not have supported extensive *C. vulgaris* growth to warrant muirburn. Cores from this site were taken adjacent to the bog pools in a *Sphagnum* dominated lawn/hummock system. Cores from the degraded site were taken adjacent to a ditch. Following sampling, the site was gully blocked as part of the ongoing restoration effort (all site descriptions *pers. comm*. Daniela Klein, RSPB, 2019).

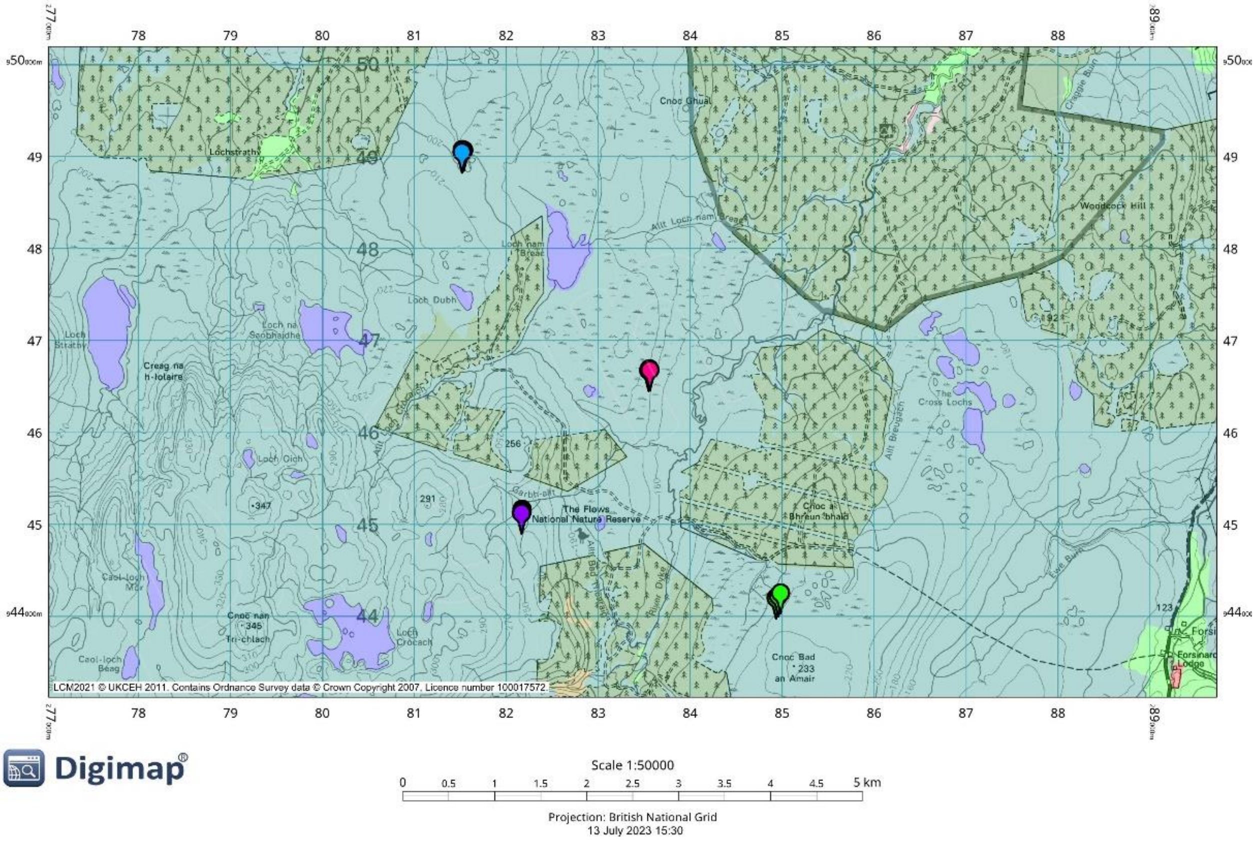


Figure 3.6 Map of mesocosm sampling sites within the Forsinard Flow Country peatland, Scotland. 10-year post restoration sites are shown in pink, 5-year post restoration in blue, degraded sites in purple, and intact sites in green. Due to the proximity of some of the sampling locations and scale of the map, not all individual sampling locations can be seen on the map.

Table 3.9 Scotland mesocosm core site descriptors. Elevation is given in meters above sea level, BNG refers to British national grid coordinates.

Management	Core	Mesocosm code	Peat depth (cm)	Slope (°)	Aspect	Elevation (AMSL; m)	BNG	Latitude	Longitude
10Y	1	S10Y1	149	4	64	176	NC8355146452	58.39093	-3.99364
	2	S10Y2	225	5	110	176	NC8356046464	58.39094	-3.99350
	3	S10Y3	313	6	104	175	NC8356646453	58.41188	-3.99339
5Y	1	S5Y1	511	2	18	201	NC8153948841	58.41183	-4.02927
	2	S5Y2	470	3	2	201	NC8152748847	58.41188	-4.02948
	3	S5Y3	359	2	10	202	NC8152348826	58.411694	-4.0295343
Degraded	1	SD1	320	1	330	234	NC8217744937	58.37697	-4.01635
	2	SD2	293	2	340	234	NC8217444915	58.37677	-4.01639
	3	SD3	280	2	336	235	NC8216944896	58.37660	-4.01647
Intact	1	SI1	257	1	270	212	NC8493543971	58.36903	-3.96874
	2	SI2	192	2	302	211	NC8496143995	58.36925	-3.96831
	3	SI3	128	4	290	236	NC8498444024	58.36952	-3.96793

Table 3.10 Vegetation surveys and images of cores in-situ prior to Scotland core collection. *Sphagnum* moss coverage included in moss % coverage. 'S' refers to Scotland, 10Y and 5Y refer to 10-years and 5-years post-restoration respectively, D to degraded plots, and I to intact plots. % vegetation coverage was recorded only for canopy cover. Three mesocosm cores collected (one larger central core and two smaller side cores). Clado refers to *Cladonia* (a lichen).

S10Y1

Vegetation type	% cover
Calluna	20
Moss	10
Sedge	65
Shrub	5
Clado	0

S10Y2

Vegetation type	% cover
Calluna	10
Moss	30
Sedge	56
Shrub	3
Clado	1

S10Y3

Vegetation type	% cover
Calluna	15
Moss	35
Sedge	45
Shrub	2
Clado	3

S5Y1

Vegetation type	% cover
Calluna	20
Moss	20
Sedge	50
Shrub	0
Clado	10

S5Y2

Vegetation type	% cover
Calluna	15
Moss	25
Sedge	55
Shrub	3
Clado	2

S5Y3

Vegetation type	% cover
Calluna	30
Moss	30
Sedge	30
Shrub	0
Clado	10

SD1

Vegetation type	% cover
Calluna	10
Moss	55
Sedge	20
Shrub	0
Clado	15

SD2

Vegetation type	% cover
Calluna	10
Moss	30
Sedge	55
Shrub	0
Clado	5

SD3

Vegetation type	% cover
Calluna	10
Moss	5
Sedge	80
Shrub	0
Clado	5

SI1

Vegetation type	% cover
Calluna	5
Moss	35
Sedge	55
Shrub	0
Clado	5

SI2

Vegetation type	% cover
Calluna	10
Moss	70
Sedge	15
Shrub	0
Clado	5

SI3

Vegetation type	% cover
Calluna	10
Moss	30
Sedge	60
Shrub	0
Clado	0

3.2.4.2 The Peak District

The sites within the Peak District used in this thesis are part of ongoing restoration projects managed by the Moors for The Future (MFF) project. Sites in the vicinity of Kinder Scout and Bleaklow were extensively grazed and there were substantial areas of bare peat until 1982 when the National Trust purchased the land (Anderson & Radford, 1984). To restore the blanket bog, policies such as grazing reduction were implemented which resulted in some plant recolonisation, but much bare peat remained. In 2002, the newly formed MFF project began restoration in the area which involved exclusion of grazing, gully blocking, and lime and fertiliser treatments for bare peat. The area was seeded with amenity grasses, dwarf shrubs, heather (*C. vulgaris*) brash, and *Sphagnum* plugs were applied (Pilkington, 2015). The sites sampled from in this thesis are part of the Making Space for Water project – a DEFRA funded project undertaken by MFF (all site information pers. comm. Michael Pilkington, MFF, 2019).

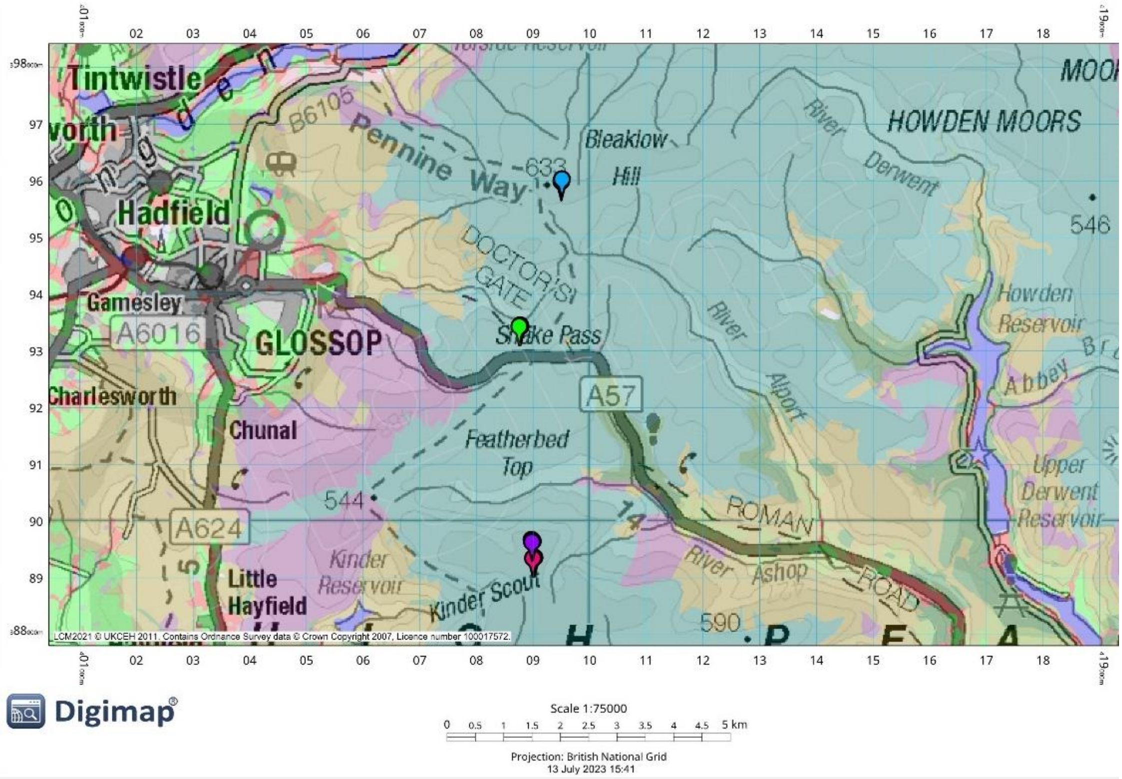


Figure 3.7 Mesocosm sampling sites in the Peak District. 10-year (10Y) post restoration sites are shown in pink, 5-year (5Y) post restoration in blue, degraded sites in purple and intact sites in green. Due to the proximity of some of the sampling locations and scale of the map, not all individual sampling locations can be seen on the map. Map made with Digimap using the 2019 land cover base map.

Table 3.11 The Peak District mesocosm site descriptors. Elevation is given in meters above sea level, BNG refers to British national grid coordinates.

Management	Core	Mesocosm code	Peat depth (cm)	Slope (°)	Aspect	Elevation (AMSL; m)	BNG	Latitude	Longitude
10Y	1	P10Y1	152	10	200	490	SK0902989020	53.39793	-1.86568
	2	P10Y2	138	4	300	547	SK0900489013	53.39787	-1.86605
	3	P10Y3	162	5	300	489	SK0900289008	53.39783	-1.86608
5Y	1	P5Y1	85	11	43	600	SK0950295652	53.45754	-1.85837
	2	P5Y2	100	6	56	616	SK0950595679	53.45778	-1.85832
	3	P5Y3	100	14	162	616	SK0951395686	53.45784	-1.8582
Degraded	1	PD1	118	0	350	615	SK0897689331	53.40073	-1.86647
	2	PD2	186	0	280	522	SK0900189307	53.40051	-1.86609
	3	PD3	135	0	120	599	SK0898389295	53.40041	-1.86636
Intact	1	PI1	241	2	338	508	SK0878393096	53.43457	-1.86926
	2	PI2	304	4	288	511	SK0877693112	53.43472	-1.86937
	3	PI3	273	5	300	514	SK0876293098	53.43459	-1.86958

Table 3.12 Vegetation surveys and images of cores in-situ prior to the Peak District core collection. *Sphagnum* moss coverage included in moss % coverage. 'PD' refers to the Peak District, 10Y and 5Y refer to 10-years and 5-years post-restoration respectively, D to degraded plots, and I to intact plots. % vegetation coverage was recorded only for canopy cover. Three mesocosm cores were collected (one larger central core and two smaller side cores).

P10Y1

Vegetation type	% cover
Calluna	10
Moss	55
Sedge	35
Bare	0

P10Y2

Vegetation type	% cover
Calluna	10
Moss	38
Sedge	50
Shrub	2

P10Y3

Vegetation type	% cover
Calluna	10
Moss	25
Sedge	65
Bare	0

P5Y1

Vegetation type	% cover
Calluna	10
Moss	40
Sedge	50
Bare	0

P5Y2

Vegetation type	% cover
Calluna	25
Moss	35
Sedge	40
Bare	0

P5Y3

Vegetation type	% cover
Calluna	5
Moss	65
Sedge	30
Bare	0

PD1

Vegetation type	% cover
Calluna	0
Moss	0
Sedge	0
Bare	100

PD2

Vegetation type	% cover
Calluna	0
Moss	0
Sedge	0
Bare	100

PD3

Vegetation type	% cover
Calluna	0
Moss	0
Sedge	0
Bare	100

PI1

Vegetation type	% cover
Calluna	1
Moss	5
Sedge	94
Bare	0

PI2

Vegetation type	% cover
Calluna	0
Moss	25
Sedge	70
Shrub	5

PI3

Vegetation type	% cover
Calluna	0
Moss	5
Sedge	95
Shrub	0

3.2.4.3 Exmoor

The Exmoor sites sampled in this thesis were managed by the Exmoor Mires Partnership, whose focus is largely on blanket bog restoration through grip blocking. The blanket bog sites sampled in this thesis were drained for agricultural development in the 19th and 20th centuries and in places underwent peat cutting. However, it is difficult to ascertain a detailed site history. In the 1800s, the degraded site was heavily drained and underwent extensive mineral prospecting, and the intact site comprises deep peat with bog pools; however, some ditches were dug to the north of the site in the 19th century.

The mesocosm locations were at 382 m – 486 m above sea level with an average minimum temperature of 5.99 °C and average maximum of 12.46 °C with 3334 mm of precipitation annually and thus, the climate of Exmoor National Park is on average warmer and wetter than other UK peatland areas (Grand-Clement *et al.*, 2013). Average peat depth is shallower than what is commonly found in the UK (1.65 m compared to ~2.85 m found in Scotland for sites sampled in this work). Unlike in the Peak District where degradation exhibits in the form of erosion and exposure of bare peat, degradation in Exmoor is a result of historical drainage, peat cutting and likely too frequent fires (especially wildfire) which has led to the dominance of *Molinia caerulea* (Grand-Clement *et al.*, 2013). Consequently, peatlands within the Exmoor National Park are thought to differ to deeper peats in their structure and function (Grand-Clement *et al.*, 2013).

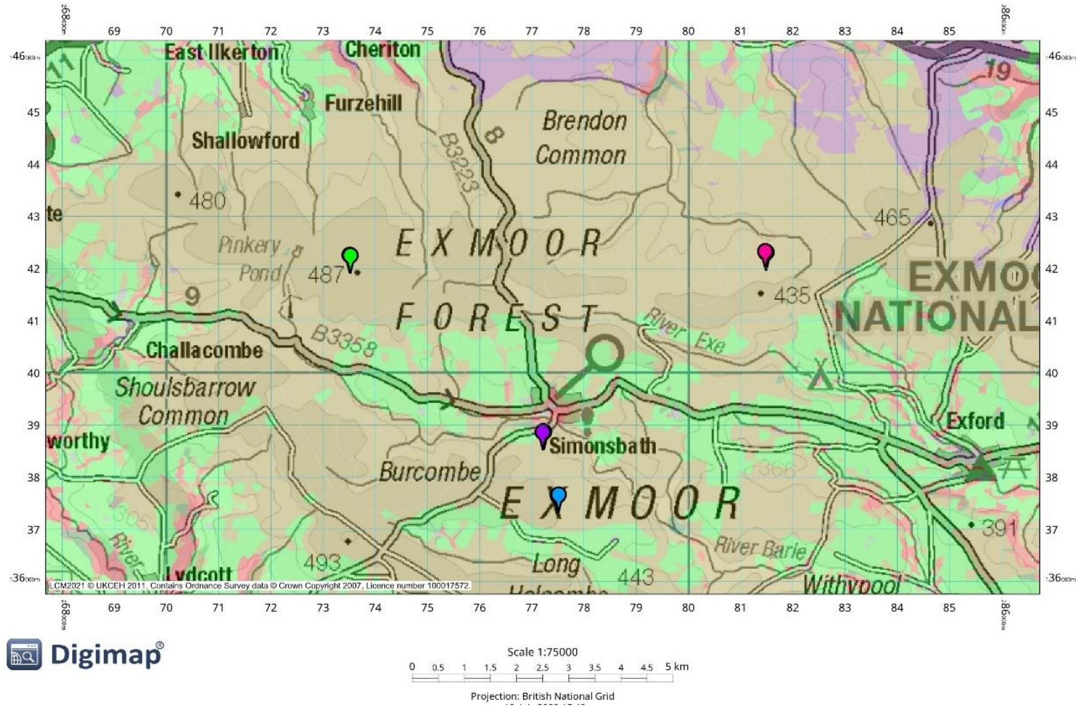


Figure 3.8 Mesocosm sampling sites in Exmoor. 10Y post restoration sites are shown in purple, 5Y post restoration in pink, degraded sites in blue and intact sites in yellow. Due to proximity of some of the sampling locations and scale of the map, not all individual sampling locations can be seen on the map.

Table 3.13 Exmoor mesocosm site descriptors. Elevation is given in meters above sea level, BNG refers to British national grid coordinates. Elevation is given in meters above sea level, BNG refers to British national grid coordinates.

Management	Core	Mesocosm code	Peat depth (cm)	Slope (°)	Aspect	Elevation (AMSL; m)	BNG	Latitude	Longitude
10Y	1	E10Y1	215	6	314	414	SS8148841963	51.1646	-3.69632
	2	E10Y2	162	4	298	414	SS8149541973	51.16469	-3.69623
	3	E10Y3	247	5	308	413	SS8148241979	51.16474	-3.69641
5Y	1	E5Y1	195	4	36	415	SS7750237306	51.1219	-3.75172
	2	E5Y2	219	5	36	415	SS7750837314	51.12198	-3.75163
	3	E5Y3	215	6	64	414	SS7751337325	51.12208	-3.75157
Degraded	1	ED1	104	5	100	383	SS7722338539	51.13293	-3.75612
	2	ED2	105	6	111	382	SS7723938531	51.13286	-3.75589
	3	ED3	100	4	112	383	SS7721638523	51.13278	-3.75622
Intact	1	EI1	134	4	68	487	SS7351641914	51.16245	-3.81026
	2	EI2	154	4	77	487	SS7352341918	51.16249	-3.81016
	3	EI3	129	4	89	486	SS7352741909	51.16241	-3.8101

Table 3.14 Vegetation surveys and images of cores in-situ prior to the Peak District core collection. *Sphagnum* moss coverage included in moss % coverage. ‘PD’ refers to the Peak District, 10Y and 5Y refer to 10-years and 5-years post-restoration respectively, D to degraded plots, and I to intact plots. % vegetation coverage was recorded only for canopy cover.

E10Y1		**E10Y2**	
			
Vegetation type	**% cover**	**Vegetation type**	**% cover**
Grass (*Molinia*)	80	*Grass (Molinia)*	90
Moss	20	Moss	10
Sedge	0	Sedge	0
Bare	0	Bare	0
E10Y3		**E5Y1**	
			
Vegetation type	**% cover**	**Vegetation type**	**% cover**
Grass (*Molinia*)	85	*Calluna*	95
Moss	15	Moss	5
Sedge	0	Sedge	0
Bare	0	Bare	0

E5Y2

Vegetation type	% cover
Grass (*Molinia*)	95
Moss	5
Sedge	0
Bare	5

E5Y3

Vegetation type	% cover
Calluna	95
Moss	5
Sedge	0
Bare	0

ED1

Vegetation type	% cover
Grass (*Molinia*)	65
Moss	20
Sedge	15
Bare	0

ED2

Vegetation type	% cover
Grass (*Molinia*)	85
Moss	15
Sedge	0
Bare	0

ED3	EI1
	

Vegetation type	% cover
Grass (*Molinia*)	70
Moss	25
Sedge	5
Bare	0

Vegetation type	% cover
Calluna	50
Moss	45
Sedge	5
Bare	0

EI2	EI3
	

Vegetation type	% cover
Grass (*Molinia*)	30
Moss	60
Sedge	10
Bare	0

Vegetation type	% cover
Grass (*Molinia*)	30
Moss	65
Sedge	5
Bare	0

3.3 Mesocosm study

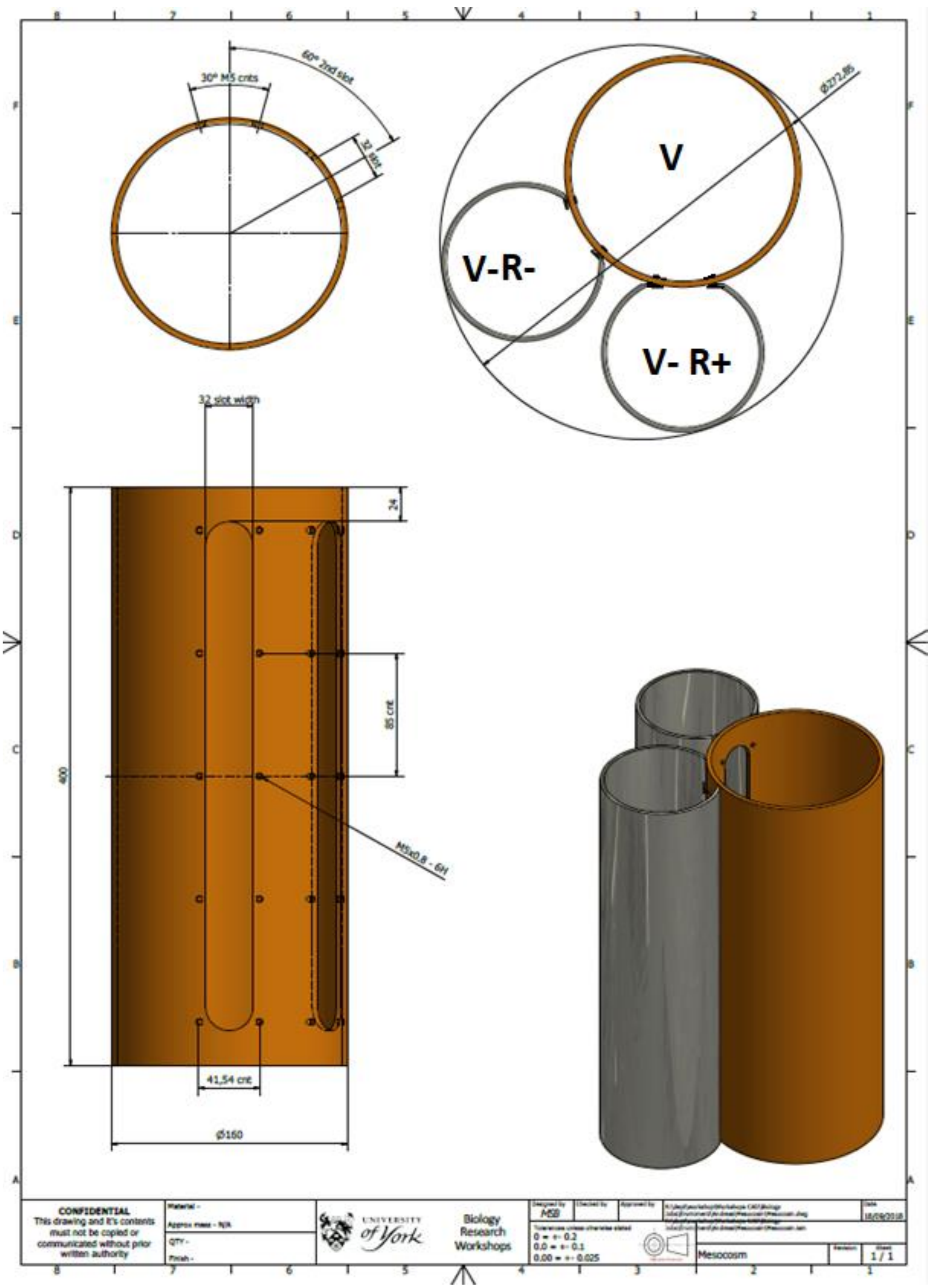
Peat mesocosms formed the bulk of the thesis' experimental and monitoring work. Mesocosms provided a logistical solution to assessing samples originating from disparate areas, allowing the examination of peat bog behaviour over a wider spatial scale, but under similar environmental conditions.

Whilst a mesocosm experiment aims to bridge the gap between field and laboratory studies, it is important to consider the limitations to this experimental design. As the cores are removed from their ecosystem (and in this case the movement from one climatic zone to another), it is possible that over time and space, the plant/soil community and processes may diverge from its original state (Dzialowski *et al*., 2014). To assess potential impacts, peat soil samples were also taken from sites which form part of the Peatland-ES-UK project (Heinemeyer, 2023) and therefore, gas flux measurements (i.e., capturing plant/soil carbon cycle processes) could be compared to those measured in the field at those sites. In addition, whilst the climate zones where the cores were taken from differed to the experimental mesocosm site in York, it is important to note that York's climate is within the average range of the range of blanket bog sites from which the cores were taken. .

3.3.1 Mesocosm design

Each mesocosm consisted of 3 cores: 1 central vegetated core and 2 flanking auxiliary vegetation free cores (Figure 3.9). The central core was used to derive plant-soil ecosystem fluxes whilst the side cores were used to obtain soil flux components: one core for soil decomposition with root fluxes and the other for only soil decomposition fluxes achieved through repeated root cutting. This partitioning method allowed quantification of the contributions to ecosystem respiration (R_{eco}) from root-derived or rhizosphere (autotrophic), soil microbial or decomposition (heterotrophic) and overall plant-soil (NEE) components.

A)



30° M5 cnts
60° 2nd slot
32 slot
Ø272,86
V
V-R-
V- R+
32 slot width
24
85 cnt
400
M5x0.8 - 6H
41,54 cnt
Ø160
CONFIDENTIAL
This drawing and it's contents must not be copied or communicated without prior written authority
Material -
Approx mass - N/A
QTY -
Finish -
UNIVERSITY of York
Biology Research Workshops
Designed by
MSB
Checked by
Approved by
Date
18/09/2018
0 = +- 0.2
0.0 = +- 0.1
0.00 = +- 0.025
Mesocosm
Revision
Sheet
1 / 1

B)

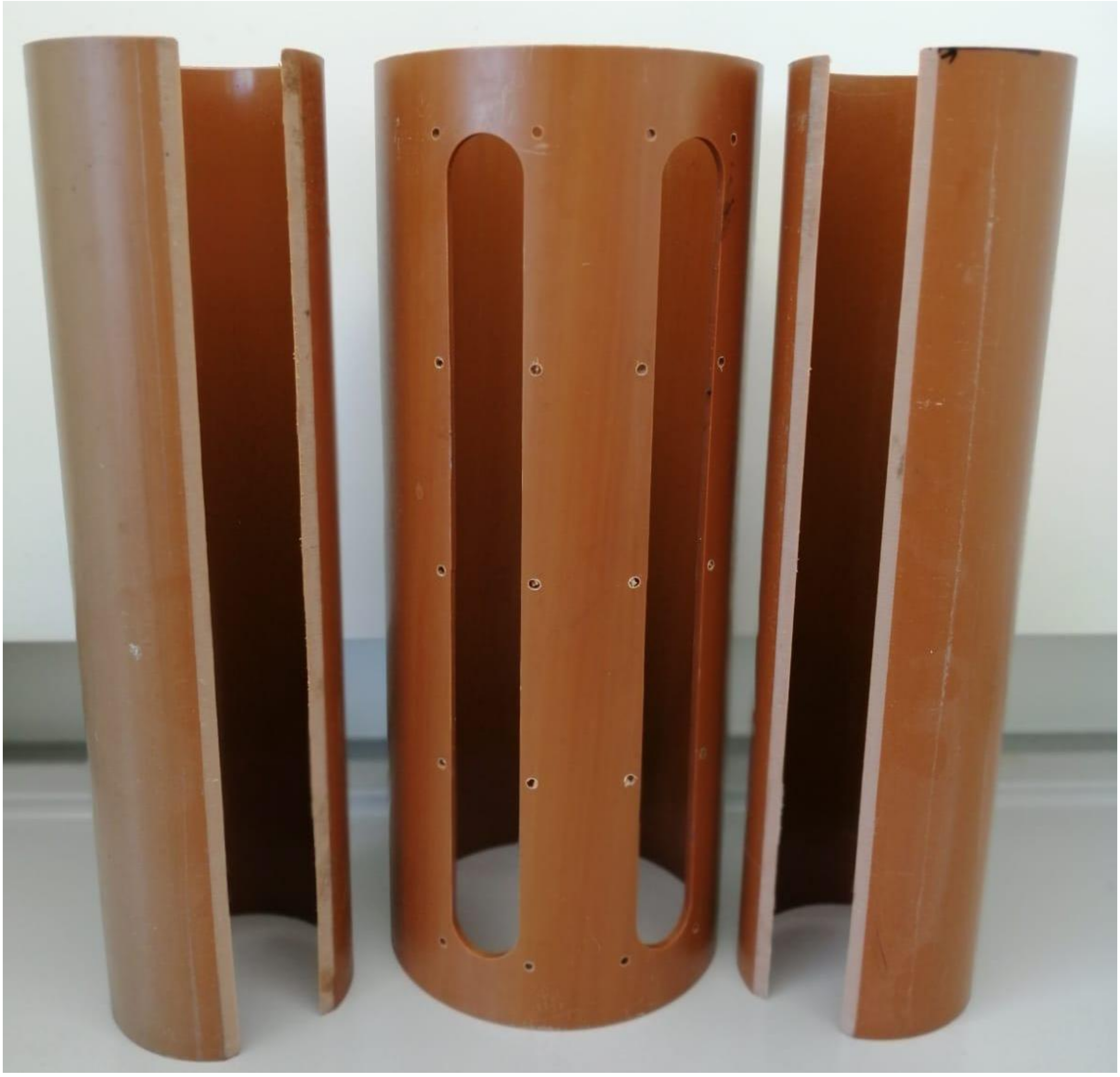


Figure 3.9 **A**) Schematic drawing of the mesocosm design. Designed by Mark Bentley, Biology mechanical workshop, University of York. Note: only the central (red) core was vegetated and whilst one of the smaller (grey) cores was cut repeatedly to sever roots, the other allowed continuous root growth. V and V- indicates the presence and absence of vegetation respectively. R+ and R- indicates the presence and absence of roots respectively. **B**) Photo of the core set up before assembly (screws inserted into the holes of the central core allowed insertion of the side cores behind the screw heads).

3.3.2 Heslington East site preparation and installation

The site on University of York, Heslington East campus (approximately LAT 53.945652, LONG -1.025128) was selected to enable easy access for maintenance, monitoring, and sampling. Three trenches were measured and dug using an excavator. Removed material was shifted by hand to remove large and sharp stones to prevent damage to the buckets. Buckets with lids were placed in the trenches equidistant as per Figure 3.10. The trenches were then backfilled by hand with the excavated material. Turf and other compostable biomass were used to fill the spaces between the mesocosms to prevent subsidence. Black anti-weed matting was placed over the trenches with holes cut for the mesocosms and secured to prevent vegetation growth around and between the mesocosms. Chicken wire mesh was cut and placed around the buckets to prevent damage to the core vegetation.

The cores were placed in 33.8 cm wide and 41.8 cm deep white plastic buckets (EZ2500-00 Wolf Plastics, Germany) and sunk into these 3 purpose-dug trenches to facilitate soil temperatures of the cores remaining comparable to soil temperatures under field conditions. To enable maintenance of a range of controlled water tables, three 5 mm circumference holes at 5 cm, 15 cm and 25 cm below the surface were installed with removable rubber bungs. To permit free drainage of the buckets when required and to prevent contact with surrounding mineral soil, a cover was fitted over the drainage holes.

To allow maintenance of water table depths, an on-site rain collection system was installed. This consisted of a 3 m x 2 m steel scaffold with a tilted corrugated plastic roof connected to three 200 L water butts (Figure 3.10). When sufficient water volumes were not available, water tables were maintained using deionised water (to avoid the addition of dissolved salts not present in rainwater) collected from the Department of Environment and Geography, University of York. White buckets were initially filled in this way, and then once during summer 2019 and once again in summer 2022.

Figure 3.10 Overview of the mesocosm site (referred to as Hes East) at the University of York Heslington East campus, including the on-site rain collection system. Rainwater is delivered to 80 L water storage butts where water is stored until required. 80 L water storage butts where water is stored until required.

A custom-made on-site weather station (AWS; using Delta T logger and sensor equipment) was installed for continuous monitoring of air temperature and photosynthetically active radiation (PAR) 1.5 m above ground level, rainfall, and soil moisture in one peat core (Figure 3.11). Soil temperature data loggers (Gemini; Tinytag Plus 2; TGP 4017) were used to measure soil temperature ~ 5cm below the peat surface in 3 mesocosms; 1 on each of the three rows of cores. In addition, three buckets containing mesocosm cores were placed above soil, each of which had soil temperature loggers to assess differences between soil temperature in buried and surface mesocosm cores at 5 cm and 10 cm below the soil surface. Water table depth was measured manually on a monthly basis and was lowered and heightened according to water table depth measured in the field at Nidderdale, Mossdale, and Whitendale.

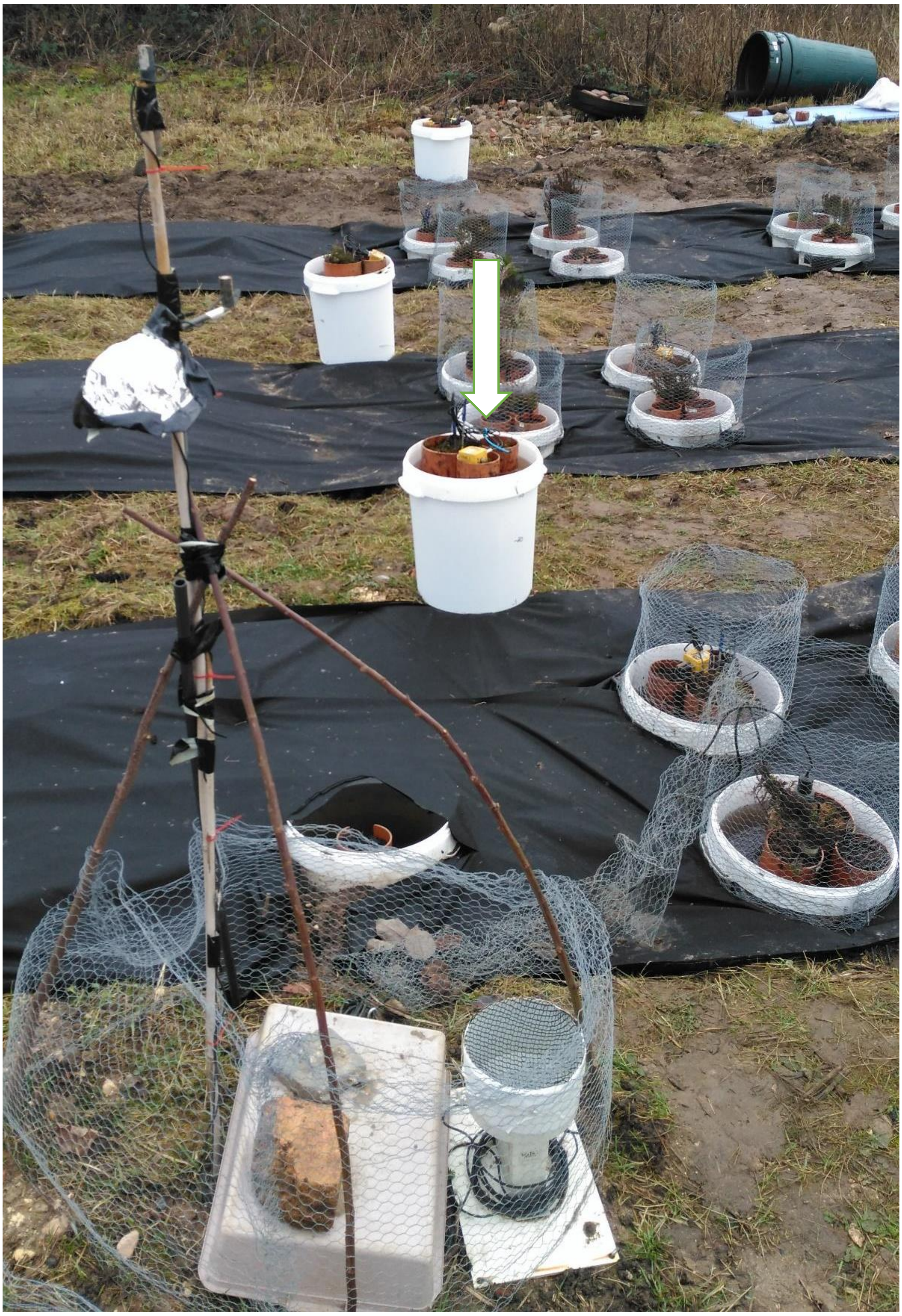


Figure 3.11 On-site (University of York, Heslington East) weather station consisting of VAR sensor (light intensity), rain gauge, wind speed gauge and air temperature sensor. Mesocosms with soil temperature probes also shown. Temperature probe indicated by arrow.

Cores were collected January 2019 – March 2019 (Table 3.15). Polyvinylchloride (PVC) tubes of 40 cm length and were driven into the peat by hand with a mallet hitting a wooden board and then lifted out with care taken to not disturb the peat cores. For the central vegetated cores, a PVC core was taped to the top of the sample core to protect vegetation prior to installation. During transportation, cores were sealed at the bottom and transported upright to prevent water loss. Where possible, cores were installed into the mesocosm buckets on arriving in York however, where this was not possible, cores were stored at 4 °C in darkness overnight and installed during the following day. Following installation of mesocosm cores, the vegetation in the uncut cores from Whitendale withered; thus, a later, second set of uncut cores were taken.

Alongside the collection of the mesocosm cores, a smaller peat soil was taken approximately 15 cm below the peat surface using a cookie cutter. Soil samples from Nidderdale, Mossdale, and Whitendale were taken on 14.02.2019 and samples from Exmoor, the Peak District, and Scotland were taken on the same day as the mesocosm cores. These were stored at 4 °C until analysis as detailed in Section 3.3.8.

Table 3.15 Collection and installation dates of mesocosm cores. *A second set of uncut cores from Whitendale were collected (NA indicates no soil cores collected on this date) due to the death of the initial core vegetation.

Site	Treatment	Collection date	Installation date	Peat soil collection
Nidderdale	All cores	14.01.2019	16.01.2019	14.02.2019
Mossdale	All cores	15.01.2019	16.01.2019	14.02.2019
Whitendale	All cores *	17.01.2019	18.01.2019	14.02.2019
	Uncut	15.05.2019	16.05.2019	NA
Scotland	10Y	20.02.2019	22.02.2019	20.02.2019
	5Y	20.02.2019	22.02.2019	20.02.2019
	Degraded	21.02.2019	22.02.2019	21.02.2019
	Intact	21.02.2019	22.02.2019	21.02.2019
Peak District	10Y	11.02.2019	13.02.2019	11.02.2019
	5Y	11.02.2019	13.02.2019	11.02.2019
	Degraded	12.02.2019	13.02.2019	12.02.2019
	Intact	11.02.2019	13.02.2019	11.02.2019
Exmoor	10Y	27.02.2019	28.02.2019	27.02.2019
	5Y	27.02.2019	28.02.2019	27.02.2019
	Degraded	27.02.2019	28.02.2019	27.02.2019
	Intact	26.02.2019	28.02.2019	26.02.2019

3.3.3 Experimental design

The mesocosm cores were arranged in a random block design throughout three trenches (Figure 3.12; see Figure 3.13 for replicate spacing). The three trenches were at different distances from the neighbouring farm access lane (Low Lane, YO10 5EF), the hedge and trees at the south of the site provided limited degrees of shade which varied daily and seasonally. The trees were deciduous and therefore did not affect the mesocosms in winter. In summer the plots were in direct sunlight for most daylight hours.

Figure 3.12 Buried mesocosms in purpose dug trenches at the Heslington East (University of York) mescosom site. Image was taken shortly after installation from the top of the rain collection system. In the centre bottom of the image, the weather station can be seen. The buckets on the soil surface are for soil temperature comparisons.

The mesocosms were arranged in blocks as seen in Figure 3.13 meaning a replicate for each site and management was present in each trench and block. As there were four replicates per management/site for the Yorkshire blanket bog sites, the fourth replicate was randomly allocated to a block.

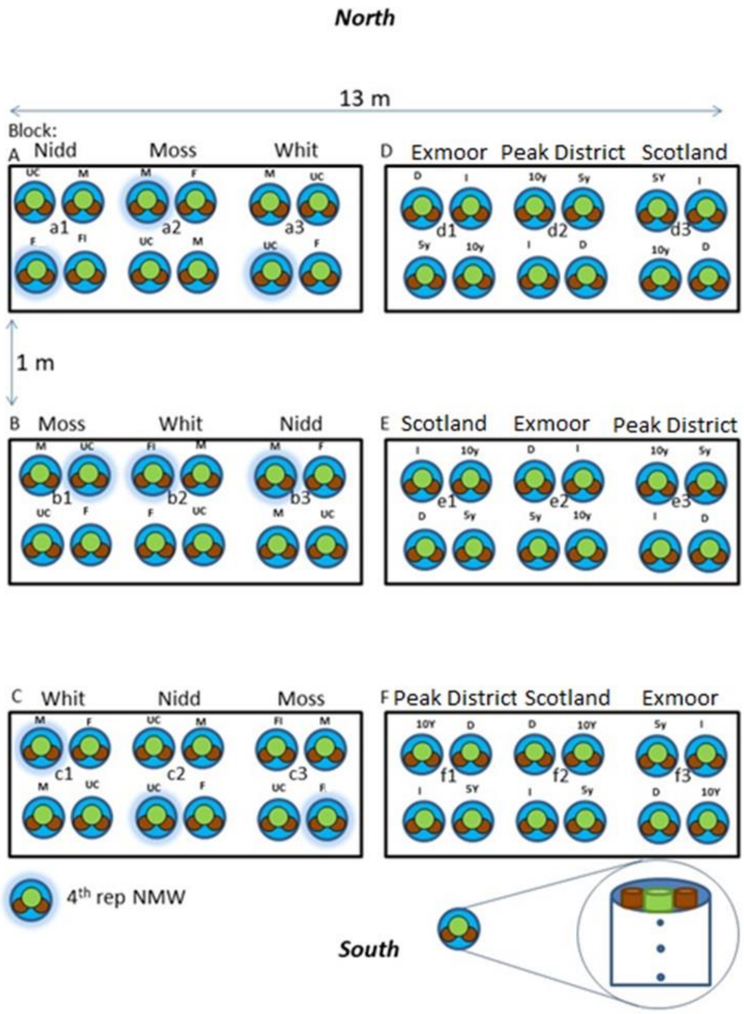


Figure 3.13 Mesocosm random block design site plan for the Heslington East (University of York) mesocosm site. F refers to burnt cores, M to mown and UC to uncut. The farm access lane is to the south of the site and the rain collection system to the north. Diagram of the mesocosm cores gives an above-view. Side-view diagram shows bung holes which can be used to alter water table depth. Shading indicates fourth replicate.

3.3.4 Rhizon samplers

Rhizon samplers (0.6 µm rhizon samplers; Rhizosphere Research Products B.V., Wageningen, Netherlands) were installed on 08.04.2019 into each mesocosm core (main and two auxilliary cores) to a depth of 10 cm to enable soil porewater collection. In dry periods and in cores where sample collection was slow, an additional rhizon was installed adjacent to the original to ensure sufficient sample volume was collected. Roughly 10% of rhizon samplers were replaced where appropriate due to wear and tear.

3.3.5 Porewater collection

Mesocosm pore water samples were collected seasonally, roughly on a 3-monthly basis. Porewater was collected using 50 mL leur-lock syringes (BD Plastipak 50 mL Leur Lok springe) attached to the rhizon samplers with a retainer holding open the syringe to create a vacuum. Samples were collected overnight and where possible during periods of lower light to prevent UV degradation of organic matter. Following collection, samples were stored in the dark at 4°C (as per Peacock *et al*., 2014 who demonstrated no sample degradation for peatland draining waters over a 12 week period) and analysed within two weeks of collection.

3.3.6 Vegetation surveys

Vegetation surveys were undertaken at the mesocosm core collection sites and on the mesocosm cores on an annual basis (Table 3.18). The initial surveys prior to removing the cores are presented within the site descriptions found in this chapter. A 1 x 1 m area with the core site in the centre was surveyed (see pictures in Section 3.2.3.1 for examples). Vegetation surveys of the mesocosm cores were conducted in September 2019, 2020, and 2021. Percentage cover was estimated visually for the exposed canopy as 100% (including any bare ground) and vegetation was recorded to the species level. Where there was an understory canopy layer, this was recorded separately, and the percentage coverage corrected to be 100 %. However, whilst some vegetation was considered individually (e.g., *C.vulgaris*), others were grouped by genus (e.g., *Eriphorum* spp.; *Sphagnum* moss), or grouped more generally (other moss, grass, brash) depending upon the known importance upon peatland ecosystem processes. The final vegetation cover categories were as follows: *C. vulgaris*, shrub, herb, sedge, *Sphagnum spp*., other moss, grass, lichen, bare and brash.

Table 3.16 Dates of annual vegetation surveys of the mesocosm cores for each year of this study.

Year		Date of vegetation survey
1	2019	18th October
2	2020	10th August
3	2021	23rd August
4	2022	14th September

3.4 Porewater analysis

Each peat porewater sample collected was analysed for parameters of water quality: DOC, dissolved organic nitrogen (DON), pH, conductivity, specific wavelength ultraviolet (UV) absorbance (SUVA) at 254, 400, 465 and 665 nm and derived ratios or indicators. Vegetated central mesocosm core pore water samples from selected collections (dependent on sample volume) were also analysed using broad spectrum UV absorbance.

3.4.1 Dissolved organic carbon (DOC) and dissolved organic nitrogen (DON)

DOC concentration was determined following methods outlined in Heinemeyer *et al* (2023). DOC concentration was measured as non-purgeable organic carbon (NPOC) using a VarioTOC (Elementar Analysensysteme GmbH, Hanau, Germany) instrument. 4.5 mL of sample was added to 4.5 mL of ultra-pure deionised water except where sample volume was too low; in those cases, 3 mL of sample was added to 6 mL of ultra-pure deionised water. A 5-point calibration of 5, 10, 20, 50, and 100 ppm C and 0, 2, 5, 10, and 20 ppm N was used using a 500 mg/L stock solution prepared with 4.4121 g sodium carbonate (Na_2CO_3; analytical grade, Thermo Scientific Chemicals), 1.0627 g potassium phthalate (KHP; analytical grade, Thermo Scientific Chemicals), 1.5179 g sodium nitrate (NaNO3, analytical grade, Thermo Scientific Chemicals), and 0.9554 g ammonium chloride (NH_4Cl; analytical grade, Thermo Scientific Chemicals) in 1 L ultra-pure deionised water. Prior to calibration standards, a run-in, and a drift (both 50 ppm C and 20 ppm N stock solution), and two blanks (ultra-pure deionised water) were run. Following the 5-point calibration, a blank and reference standard (calibration stock solution 50 ppm C and 10 ppm N) were run followed by samples with a drift (20 ppm calibration standard) and blank after every 12 samples for instrumental quality control. After running all samples, a drift, blank and hydrochloric acid were run. All vials were acidified using 100 µL 0.1 M HCl and spared with oxygen for one minute to remove inorganic carbon. Operating temperature and outlet pressure were set to 850°C and 1.0-1.2 bar pressure. The oxygen inlet pressure was set to 950-1000 mbar. Sample volume was 0.250 mL. Samples were analysed three times and a mean concentration calculated. Where results were erroneous, samples were re-ran if volume was sufficient or results removed from the subsequent analysis as a quality control measure.

3.4.2 pH

pH was measured using a Thermo Orion Bench-top pH meter (model 420) which was calibrated with laboratory standard buffers of pH 2, pH 4 and pH 7 (Fisher brand Scientific). Prior to each measurement, the probe was rinsed with deionised water and lightly dried using lab paper towels. Samples were analysed at room temperature and measurements replicated three times and a mean calculated. Missing measurements are due to sample volume being too low (< 5 mL) to achieve a reading.

3.4.3 Conductivity

Conductivity was measured using a Thermo Orion Star A2/2 benchtop conductivity meter calibrated with an 84 $\mu S\ cm^{-1}$ calibration standard (Reagecon, ISO 17025 Acredited). Prior to each measurement, the probe was rinsed with deionised water and lightly dried as for pH. Samples were analysed at room temperature and replicated three times and a mean calculated. Missing measurements are due to sample volume being too low (< 5 mL) to achieve a reading.

3.4.4 UV-vis absorption

UV-vis absorbance was measured using a Shimadzu UV-2600 instrument, slit width 1.0 nm at 254, 400, 465 and 600 nm wavelengths (UV 254, 400, 465 and 665, respectively), enabling calculations of specific ultra-violet absorbance (Equation 2.1), E4/E6 ratio (UV465/UV665) and Hazen (Equation 2.2); all of which are used within the water industry as water quality indicators (as per Heinemeyer *et al*., 2019). Measurements were replicated three times and a mean calculated. Where erroneous results were obtained, samples were rescanned or excluded from the data set. A blank of ultra-pure water was used.

Equation 2-3-1 Calculation for specific ultraviolet absorbance (SUVA; $L^{-1}\,mg^{-1}\,m^{-1}$) using 254 nm absorbance (UV_{254}).

$$SUVA_{254} = \frac{UV_{254}\ absorbance}{DOC\ concentration} * 100$$

Equation 2.3-2 Calculation for hazen using UV_{400} absorbance.

$$Hazen = UV_{400\ absorbance} * 12 * 100$$

Broad spectrum UV-vis absorbance scanning was performed using a Shimadzu UV-2600, slit width 1.0 nm at 1 nm increments over a wavelength range of 230 – 800 nm with a medium scan speed. Each sample was scanned three times and the average absorbances recorded. Where erroneous results were obtained, samples were rescanned or excluded from the data set. The baseline was corrected with an ultra-pure deionised water blank prior to running any samples.

3.5 Soil analysis

Soil samples taken alongside mesocosm cores were analysed for bulk density (BD), soil moisture (SM), % organic carbon (%C_{org}), carbon/nitrogen ration (C:N). Extractable dissolved organic carbon was analysed for the water quality parameters detailed in Section 3.3.7.

3.5.1.1 Bulk density

A small cuboid/cube of soil (~ 2 cm^3) was cut from the ‘cookie cutter’ soil sample taking care to not compress the soil using a scalpel (Swann Morton, Sterile disposable scalpel No.10 with polystyrene handle). Dimensions were measured, and volume calculated using Equation 3.1. A crucible (~10-30 mL) was weighed before and after the addition of the sample and dried at 105 °C. The crucible and dry sample was subsequently weighed, the dry sample mass (Equation 3.2) and sample volume were used to calculate bulk density (Equation 3.3). Due to available sample volume, this analysis was undertaken once per sample. Due to available sample volume, this analysis was undertaken once per sample. Whilst more subsamples would enable more confidence in the results and identification of erroneous results, this would have been pseudo replication as replicates per mesocosm treatment were undertaken.

Equation 3-3 Sample volume calculation (cm^3)

$$\boldsymbol{Sample\ volume\ (cm^3) = \ length\ side\ 1\ x\ length\ side\ 2\ x\ length\ side\ 3}$$

Equation 3-4 Dry sample mass (g) calculation

$$\boldsymbol{Dry\ sample\ mass\ (g) = Crucible\ mass\ (g) - Crucible\ \&\ dry\ sample\ mass\ (g)}$$

Equation 3-5 soil bulk density (g cm^3) calculation

$$\boldsymbol{Bulk\ density\ (g\ cm^3) = \frac{Dry\ soil\ mass(g)}{sample\ volume\ (cm^3)}}$$

3.5.1.2 Soil moisture

Soil moisture was calculated using information obtained through bulk density analysis using Equation 3.4.

Equation 3-6 Soil moisture (%) calculation

$$\boldsymbol{Soil\ moisture\ (\%) = \frac{Dry\ soil\ mass\ (g)}{Wet\ soil\ mass\ (g)}\ x\ 100}$$

3.5.1.3 % organic carbon and nitrogen

Dried samples (see Section 3.3.8.1) were finely ground using a ball mill and analysed by an elemental analyser (Vario MACRO cube, Elementary, Germany). Each sample was analysed three times for quality control and an average calculated. Where erroneous results were obtained, where sample volume allowed, samples were analysed or excluded from the data set.

3.5.1.4 Carbon nitrogen ratio

C:N ratios were calculated as mass ratios using data obtained by methods detailed in Section 3.5.1.3.

3.5.1.5 Water extractable dissolved organic carbon

Fresh peat (3 ± 0.1 g; sampled at the time of mesocosm collection) was added to 27 mL ultrapure water and manually homogenised for 60 seconds and left for 4 hours. pH of the soil solution was then measured (as detailed in Section 3.4.2). The solution was filtered using 0.60 µm Rhizon samplers (as detailed in Section 3.3.4) and stored in the dark at 4°C until further analysis which took place within two weeks. The filtered solution was then analysed for water quality parameters (as detailed in Sections 3.4).

3.5.1.6 Soil elemental analysis

The protocol followed was outlined in a PhD thesis by Morton (2016) and is described here in brief. Approximately 0.5 g of freeze-dried ball-mill ground peat (sampled in February 2019) was placed in a 100 mL digestion tube which were transferred to a fume cupboard. 10 mL of 70% AnalaR Nitric acid was added to each tube and left overnight. Digested peat was filtered (using 0.7 µm glass fibre filter papers; Fischer Scientific) and diluted by a factor of 2 with ultrapure water. Nitric acid blanks were prepared, and the mean blank concentrations were subtracted from measured sample concentrations. Tubes were then heated in increasing increments of 10 °C until the heating block was 60 °C where it remained for three hours. Temperature was then increased incrementally to 110 °C. After six hours, the tubes were removed and left to cool overnight. 5 mL of ultra-pure deionised water was added to each tube and each sample was filtered with ashless filter paper into a centrifuge tube. This was then rinsed with ultra-pure water and the samples refiltered with a clean filter paper into volumetric flasks. This was then made up to 100 mL with ultra-pure water.

10 mL of sample was mixed with 10 mL ultra-pure water in clean sample tubes. Blanks and washes were made of nitric acid and for instrument quality control, ran every 12 samples. The standards used were Certipur ICP multi-element standard solution IV (Merck KGaA, Germany) with the additional of Trace-cert Arsenic Standard for ICP (Sigma Aldrich LLC, USA). 14 elements (nutrients of ecological/environmental importance: Cu, Zn, Pb, Al, Ca, Fe, K, Mg, Na, Mn, Cd, P, As, and Si) were measured using Inductively Coupled Plasma (ICP) with an ICP-7000 (ICP-OES instrument). Each sample was analysed three times and a mean calculated. Where an erroneous result was obtained, the sample was excluded.

3.6 Gas flux methodology

Mesocosms were monitored for gas fluxes, namely net ecosystem exchange (NEE), soil respiration (SR) and methane (CH_4) fluxes. The methods described here are given in more detail in Heinemeyer *et al*. (2019). Gas flux measurements were taken on dates listed in Table 3.19.

Table 3.17 Dates of gas flux measurements on mesocosm cores, Heslington East (University of York). Up to 21st July, Licor 8100 analyser was used. Measurements taken on Jul 21st and onwards were taken using LiCor 7810 greenhouse gas analyser.

	Year	Date	Number of measurements
Net ecosystem exchange and methane flux	2019	1st August 23rd October 29th October 3rd December	n = 13
	2020	5th February 21st July 15th October	
	2021	6th May 15th June 10th November	
	2022	17th January 5th May 3rd October	
Soil respiration	2019	29th July 15th August 12th September 24th October 2nd December	n = 14
	2020	6th February 22nd July 14th October	
	2021	16th June 9th November 7th may	
	2022	6th February 18th January 3rd May	

3.6.1.1 Soil respiration

SR measurements were taken in the two-vegetation free mesocosm side cores using a Li-Cor 8100 Infrared Gas Analyser (IRGA) connected to a 10 cm automated survey chamber (model 8100-102, LI-COR, Lincoln, NE, USA). CO_2 concentration was measured every second for a period of 45-60 seconds (dependent on season). Flux was derived from the most linear portion of the measurement based on the R^2 value using Li-Cor viewer software (Li-Cor Biosciences). Fluxes were corrected for air temperature and pressure, water vapour, chamber volume and surface area during data processing. SR was measured as total SR including soil + root fluxes (i.e., SR_{tot}; uncut side cores) and soil decomposition flux only (i.e., SR_{cut}; cut side cores).

3.6.1.2 Net ecosystem exchange

NEE measurements were taken on each central vegetated mesocosm core. Custom made Perspex© chambers were made by the University of York Biology Workshop to allow for measurement of vegetation of different heights (9 cm, 25 cm and 55 cm). A battery-operated computer fan (~6 cm diameter fitted below the middle chamber height - when measuring this part was facing away from the sun) was placed inside the chamber to facilitate adequate chamber air mixing. Chambers were connected to an IRGA (Model 8100, LI-COR, NE, USA) and fitted with a photosynthetically active radiation (PAR) sensor (Q55-PAR Quantum Sensor, Delta-T Devices, Cambridge, UK) fitted to the LI-COR auxiliary sensor interface and placed inside the chamber using a custom 3D printed widget with a magnetic plate (Biology Workshop, University of York). An air temperature sensor (part of the LiCor gas flow cable) was inserted into the chamber along with in- and out-flow tubing. Gas concentrations were corrected using air temperature and moisture by the LiCor processing software (viewer) and CO_2 fluxes were calculated using dry CO_2. Where measurements appeared erroneous (potentially due to a break in the chamber-soil seal or an air pocket), measurements were retaken as a quality control measure.

CO_2 concentration within the chamber was measured once per second for 45 – 90 seconds depending on light levels and air temperature (measurements in cooler periods were longer). Measurements for 3 (and later on 4) light levels (by sequentially placing layers of horticultural shading mesh to shade and finally a black ground sheet cover hood to block all light) were taken (Table 3.20). The resulting fluxes under different light levels allow fitting of light response curves and therefore calculation of the light compensation point (LCP) of photosynthesis (see methods in Heinemeyer *et al*., 2019) and fluxes in the dark provide ecosystem respiration (R_{eco}) fluxes.

Table 3.18 Light (measured as photosynthetic active radiation; PAR) levels of net ecosystem exchange measurements.

Light (PAR) level	% of light (PAR)	Measurement taken with shading lowering (<) or increasing (>) the proportion of a flux component
Full light	100	Photosynthesis and respiration
Low shade	71.5	<Photosynthesis & >respiration
High shade	~	<<Photosynthesis & >>respiration
Dark	0	Ecosystem respiration (plant and soil respiration)

CO_2 fluxes were derived using LI-COR viewer software using the most linear 40-60 seconds portion of the measurement for each light level. All fluxes were corrected for chamber volume and surface area, temperature, and pressure. Fluxes were expressed in µmol CO_2 m^{-2} s^{-1}.

3.6.1.3 Net ecosystem exchange and soil respiration partitioning

Using methods as detailed in Heinemeyer *et al*. (2019), the combination of NEE and SR with and without root flux measurements allowed the total NEE, R_{eco} and SR fluxes to be partitioned into photosynthesis (vegetation) and respiration from soil (Equation 3.1- 3.3). These values were then used to derive respiration components with which were subsequently used to derive key carbon balance parameters. Thus, gross primary productivity (GPP; Equation 3.4), net primary productivity (Equation 3.5), and carbon use efficiency (CUE; Equation 3.6).

Equation 3-7 Equation for the calculation of root respiration (R_{root})

$$\boldsymbol{Root\ respiration\ (Rroot) = Total\ soil\ respiration\ (SRtot) - Soil\ respiration\ of\ cut\ side\ core\ (SRcut)}$$

Equation 3-8 Equation for shoot respiration

$$\boldsymbol{Shoot\ respiration\ (Rabove) = Ecosystem\ respiration\ (Reco) - below\ respiration\ (Rbelow)}$$

Equation 3-9 Equation for the calculation for microbial respiration (Rmic)

$$\boldsymbol{Microbial\ respiration\ (Rmic) = SRcut}$$

Equation 3-10 Equation for gross primary productivity (GPP).

$$\boldsymbol{Gross\ primary\ productivity\ (GPP) = Net\ ecosystem\ exchange\ (NEE) - Ecosystem\ respiration\ (Reco)}$$

Equation 3-11 Equation for net primary productivity (NPP)

$$\begin{aligned}\boldsymbol{Net\ primary\ productivity\ (NPP)}\\ = \boldsymbol{Gross\ primary\ productivity\ (GPP) - Vegetation\ respiration\ (Rveg)}\end{aligned}$$

Equation 3-12 Equation for carbon use efficiency (CUE)

$$\boldsymbol{Carbon\ use\ efficiency\ (CUE)} = \frac{\boldsymbol{Net\ primary\ productivity\ (NPP)}}{\boldsymbol{Gross\ primary\ productvity\ (GPP)}}$$

3.6.1.4 Methane Flux

Methane (CH_4) measurements were measured as part of the NEE and SR fluxes (i.e., from the same chambers). This was initially done using an Ultraportable Greenhouse Gas Analyser (UGGA; Los Gatos Research, USA; measurements taken in 2019), but from the 21st of July 2020 onwards, a LiCOR 7810 GHG analyser (LiCor Biosciences, USA) was used. The analyser was connected to the flux chambers via tubing (Bev-a-line IV, Thermoplastic Processes Inc., USA) as part of a closed loop sub-sampling system. Fluxes were viewed in real time via a tablet-computer (to allow spotting accidental ebullition [gas bubbles increasing concentrations with subsequent decline due to mixing], which was followed by venting the chamber and remeasuring). CH_4 flux was calculated using the LiCor Soil Flux Pro 4.2.1 software (by combining LiCor fluxes with CH_4 fluxes based on a timestamp) in nmol CH_4 m^{-2} s^{-1}. The flux calculations were corrected using the same variables as listed for NEE and SR. Where measurements appeared erroneous (potentially due to a break in the chamber-soil seal or an air pocket), measurements were retaken as a quality control measure.

3.7 Drinking water treatment analysis

All water samples discussed in this chapter were obtained from peat mesocosms using methodology as detailed in section 3.3.5. Prior to chlorination, samples were tested for DOC, pH, and UV-vis absorption (see Section 3.4) as part of investigations into the effects of management regime and restoration upon blanket bog water quality (Chapter 4 and 5 respectively).

3.7.1 Sample selection

92 samples were selected to be analysed to test the hypotheses stated in section 7.1 based on water quality parameters discussed in Chapter 4, 5, and 6 and where sample volumes were sufficient for analyses. Samples were frozen at -20 °C following water quality testing until the further analysis detailed in this chapter was undertaken. Additional sampling (November 2022) was done to ensure sufficient sample volume and number for DBPFP and chemical group analysis. Each sample was extracted once due to available sample volume. Whilst more subsamples would enable more

confidence in the results and identification of erroneous results, this would have been pseudo replication as replicates per mesocosm treatment were undertaken along with analysis of the same core over the sampling time-period (where sample volume permitted).

3.7.2 Disinfectant by-product formation sample preparation

Sample preparation and subsequent analysis detailed below are based upon the standardised methodology detailed in US EPA 'Enhanced Coagulation and Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual' (1999) and EPA methodology 551.1 and 553.2, and within the literature (e.g., Ritson (2015), Ritson *et al* (2016)) with additional guidance provided by Yorkshire Water (pers comms with Jenny Banks, technical specialist).

3.7.2.1 Chlorine solution preparation

3.55 mL of 14 % sodium hypochlorite (King Scientific, reagent grade) was added to 500 mL of ultra-pure water giving a concentration of 1 g L^{-1} chlorine. This was made fresh for each incubation.

3.7.2.2 Phosphate buffer preparation

68.1 g potassium dihydrogen phosphate (KH_2PO_4; Sigma Aldrich, >99 % purity) and 11.7 g sodium hydroxide (NaOH; Sigma Aldrich > 98 % purity), were added to 1 L ultra-pure water. A magnetic stirrer was used to ensure dissolution. Buffer was stored in an airtight glass container and refrigerated at 4 °C and was discarded after 7 days.

3.7.2.3 Sample incubation

Water samples were left to reach room temperature following storage and refrigeration/freezing (4 °C and -20 °C respectively; as per section 8.3 EPA 551.1). Each sample was diluted with ultra-pure water to a 1:10 solution due to available sample volume. Sample pH was measured using a Thermo Orion Bench-top pH meter (model 420) and adjusted to pH 7 using NaOH 0.1 M. Following the methods as stated in EPA Method 555.1, phosphate buffer solution (1.25 mL) was added per 50 mL of diluted sample. The sample was chlorinated (using the chlorine solution detailed in Section 7.2.2.1) to a concentration of 5 mg L^{-1} Cl mg^{-1} DOC (to provide excess chlorine as per the methodology of Bond (2009) and pers comms with the specialists at Yorkshire Water). After two minutes, free residual chlorine was tested using a diethyl-p-phenylene diamine (DPD) test (Section 3.7.2.4). Samples were transferred to amber bottles and stored at room temperature (~ 20 °C) for 7 days, after which sodium thiosulphate crystals (Sigman Aldrich, = 99.99% purity) were added to the samples to quench any further reaction with chlorine.

3.7.2.4 Diethyl-p-phenylene diamine test for free residual chlorine

According to methodology outlined in EPA-NERL 330.5, 1 mL of chlorinated sample was removed and added to 9 mL ultra-pure water. A diethyl-p-phenylene diamine (DPD; Thermo Scientific Orion AQUAfast II) was added to the solution and dissolved. The colour produced was compared to a calibrated colour chart supplied with the DPD test.

3.7.3 Trihalomethane analysis

3.7.3.1 Trihaloemethane sample extraction

Seven days following incubation, samples were checked to verify their pHs were within 4.5-5.5. If a sample was outside this range, it was discarded based on quality control from literature reports of effective removal for ferric sulphate (coagulant during drinking water treatment; Matilainen *et al*., 2005). 60 mL glass vials were weighed (to enable subsequent volume determination) and 30 mL of chlorinated sample was added to the vials. Subsequently, 2 mL methyl tert-butyl ether (MTBE; (Sigma-Aldrich, 99.9% purity) was added to each vial, along with 50 µL of internal standard (bromoflurobenzene at 1000 µg mL^{-1} in methanol; Supelco) and 10 g of sodium sulphate (anhydrous, > 99% purity, Scientific Laboratory Supplies). Vials were hand-shaken for 4 minutes and rested for a minimum of a further 2 minutes to allow the layers to separate. Approximately 1 mL of the top (MTBE) layer was transferred to a 2 mL autosampler vial (Agilent, amber screw top vial) for analysis by gas chromatography coupled with mass spectrometry (GC-MS).

3.7.3.2 Trihalomethane sample analysis

THMs were analysed on two GC-MS instruments as the initial instrument used was replaced over the course of the study. The first instrument was a PerkinElmer Clarus 680/600C GC-MS. Instrument control and data processing was by Turbomass software. The second instrument was an Agilent 8890/5977B GC-MS fitted with a 7693A autosampler. Instrument control and data processing was with MassHunter software. The same method conditions and chromatographic columns were used on both instruments, following the protocol of EPA method 555.1 and was not validated due to it being a published, standardised methodology.

The GC injector temperature was set to at 200°C and the MS transfer line, source, and quad temperatures were set at 250°C, 230°C, and 150°C, respectively. The injection volume was 1 µL and the inlet operated in split mode with a split ratio of 5:1. After sample injection the autosampler needle was washed with water (to remove salts) followed by acetone and MTBE. A capillary column (ZB-5MS column (Phenomenex, UK), 30 m length × 0.25 mm i.d. × 0.25 µm film thickness) was used with helium carrier gas at a constant flow rate of 1 mL min^{-1}. The initial oven temperature was 35 °C held for 5 min, followed by a 20°C per min temperature ramp to 260 °C and then held for 4 min. The MS was operated in SIM mode, monitoring *m*/*z* 83 for trichloromethane (TCM), 173 for bromoform, and 95 for the internal standard bromofluorobenzene. Some samples were also run with an MS scan between *m*/*z* 46 and 400. This was to confirm peak identity (using the NIST 2020 v2.4) and to determine if other DBPs (outside of THMs) were present in the sample. The MS filament was switched off for the first 3 min of the analysis until the injection solvent had eluted. Individual SIM ion chromatogram peak areas were used to determine sample THM concentration. Each sample was analysed 3 times and a mean concentration calculated.

Calibration standards were prepared from a stock solution of a 1 g L^{-1} trihalomethane calibration mix (containing chloroform, bromodichloromethane, bromoform, and dibromochloromethane; Sigma-Aldrich EPA 501/601, TraceCert, 2000 µg mL^{-1} in methanol, 1 mL ampoule) at concentrations of 10 000 µg L^{-1}, 1000 µg L^{-1}, 100 µg L^{-1}, 10 µg L^{-1} and 1 µg L^{-1} in MTBE. Calibration standards were spiked with 50 µL of the internal standard bromoflurobenzene at 1000 µg mL^{-1} in methanol (ACS reagent, ≥99.8 %). A linear calibration curve was used, and the line of best fit was forced through 0,0 (Figure 3.14).

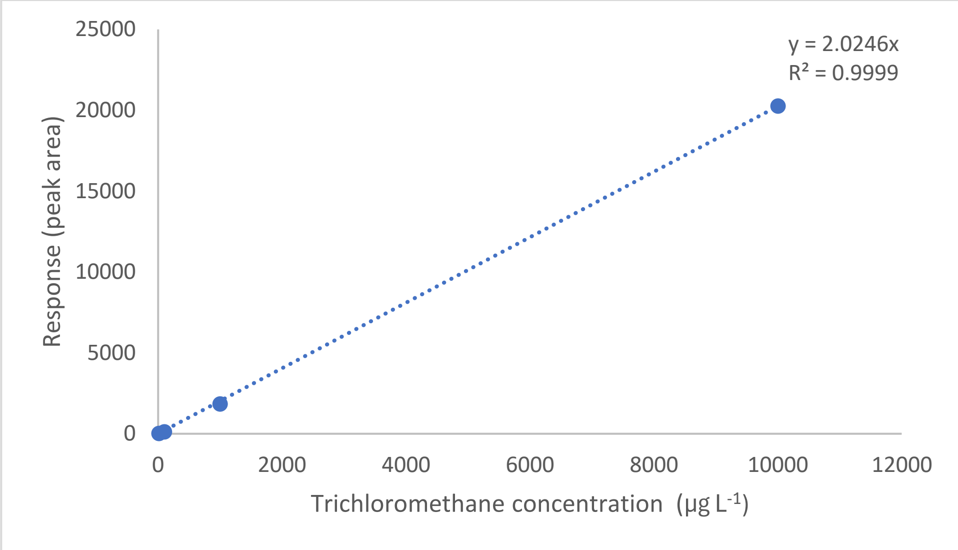


Figure 3.14 Linear calibration curve for trichloromethane used in the quantification of sample concentration. Line equation and R^2 value shown.

All samples and calibration standards were blank corrected, following EPA method 555.1 . Relative response factors (RRF) were determined for the target compounds vs the internal standard using Equation 3.13, enabling quantification of the target analyte concentration in the samples:

Equation 3-13 Calculation of relative response factor (RRF)

$$RRF = \frac{(A_s)(C_{is})}{(A_{is})(C_s)}$$

Where: RRF = Relative response factor

A_s = Response for the analyte to be measured

A_{is} = Response for the internal standard

C_{is} = Concentration of the internal standard (µg L^{-1})

C_s = Concentration of the analyte to be measured (µg L^{-1})

3.7.4 Haloacetic acid analysis

3.7.4.1 Haloacetic sample extraction

Sample extraction was followed as per EPA methodology 552.3. Following sample incubation as per Section 7.2.2.3, 30 mL of sample was removed into a glass vial (Sigma Aldrich) with a PTFE septum lid. 20 µL of surrogate solution (20 µg mL^{-1} of 2-bromobutanoic acid in MTBE; Sigma Aldrich, 97 % purity) was added to the sample which was then inverted to ensure mixing. Subsequently, 0.1 M sulphuric acid (Sigma Aldrich, ACS grade) was added (approximately 1.5 mL) to achieve pH ≤0.5, and 3 mL MTBE with an internal standard (1,2,3-trichloropropane at 300 µg L^{-1}; Thermo Scientific, purity > 98%) was added followed by 12 g sodium sulphate (anhydrous, >99 % purity, Scientific Laboratory Supplies). The solution was shaken for 3 minutes vigorously by hand. Vials were then stored on their sides to prevent clumping of the salt, and the layers formed were left to separate for approximately 5 minutes. 1 mL of the top layer was transferred to a new glass vial, along with 1 mL of 10% sulphuric acid/methanol solution (Sigma Aldrich, ACS-grade, ≥99.9 %). Vials were tightly capped and placed in a water bath at 50 °C for exactly 2 hours; on removal they were left to cool to room temperature. 1 mL of MTBE (Sigma Aldrich, 99.9 % purity) was added along with 3 mL of 10% sodium sulphate solution, and the sample was then vortexed for 30 seconds. Approximately 1 mL of the MTBE top layer formed was added to a GC vial (Agilent, amber screw top vial, 1 mL) to be analysed. Relative response factors (RRF) were determined for the target compounds vs the internal standard following Equation 3.13 (Section 9.7 in EPA 552.3), enabling quantification of the target analyte concentration in the samples

3.7.4.2 HAA analysis

The method for HAA analysis, following the protocols of EPA method 552.3, used the same instrument and conditions as above in Section 7.2.5.3, with the exception of the oven program, which had an initial temperature of 35°C (hold 8 min) before increasing it to 200°C at a rate of 8°C min^{-1} with a final hold time of 1 min. SIM ions *m/z* 59 (methyl esters of haloacetic acids) and 75 (1,2,3-trichloropropane) were monitored.

3.7.4.3 HAA calibration

Calibration standards were prepared from a stock solution of halogenated acetic acids mix containing bromoacetic, bromoachloroacetic, chloroacetic, dibromoacetic, dichloroacetic, and triachloroacetic acid (EPA 552; 2000 µg mL^{-1} of each component in MTBE; TraceCERT; Sigma Aldrich) of 1 g L^{-1} at concentrations of 100,000 µg L^{-1}, 50,000 µg L^{-1}, 25,000 µg L^{-1}, 10,000 µg L^{-1}, 1000 µg L^{-1}, 100 µg L^{-1} in MTBE. Calibration standards were spiked with 50 µL of 1000 µg L^{-1} internal standard (1,2,3-trichloropropane; Thermo Scientific, purity > 98%) made in methanol. Calibration standards were subjected to the methylation procedure as described in section 3.7.4.1. Relative response factor was used to determine sample concentration according to equation 3.13 (section 10.2.3 of EPA 552.3).

3.7.5 Acetate and formate analysis

5.5 mL of sample was filtered using a 0.2 µm nylon filter and analysed on a Dionex ICS 2000 ion chromatograph with an AS40 autosampler, ECG III KOH eluent generator cartridge, ASRS 600 2 mm suppressor and DS6 heated conductivity detector. The column used was a Dionex IonPac AS18 (2 mm id x 250 mm L) analytical column fitted with an IonPac AG18 (2 mm inner diameter x 50 mm L) guard column. The eluent was aqueous hydroxide with a linear gradient from 2 mM hydroxide to 41 mM hydroxide over 30 min at a flow rate of 0.25 mL min^{-1}. The suppressor current was set to 26 mA and the column and detector temperatures were 30°C and 35°C respectively. The sample injection volume was 15 µL. Samples were analysed for acetate, formate, chloride, nitrate, and sulphate. Commercial standards (Sigma Aldrich, *Trace*Cert, 1000 mg L^{-1}) in water were used to prepare calibration curves in the following ranges: acetate and formate (0.05 - 10.0 mg L^{-1}), chloride (1-200 mg L^{-1}), nitrate (0.02-2.0 mg L^{-1}), sulphate (0.1-5.0 mg L^{-1}), and phosphate (0.2-10.0 mg L^{-1}). Components were identified based on their retention time and quantified on the basis of their chromatographic peak areas. Instrument control and data processing was by Chromeleon software (Thermo Fisher Scientific). Samples were analysed three times for quality control and a mean value taken.

3.7.6 Chlorine reactivity and differential UV absorbance

Samples were diluted to 1:10 with 9 mL ultra-pure water. UV-vis absorbance was measured using a Shimadzu UV-2600 instrument, slit width 1.0 nm at 230 nm – 400 nm under a fast speed scan. Samples were chlorinated with 1 g L^{-1} chlorine solution (detailed in Section 7.2.2.1) at a concentration of 5 mg^{-1} 1 mg L^{-1} DOC at pH 7 in the presence of 0.03 mol L^{-1} phosphate buffer (see Section 7.2.2.2) and left for two hours. UV absorbance at 230 nm – 400 nm was remeasured and then again at 24-, 48-, 72-, and 120-hours post chlorination. The difference in absorbance was investigated as a potential indicator of chlorine reactivity and is shown in Equation 7.1. Measurements were replicated three times, a mean calculated and a blank of ultra-pure water used.

Equation 3-14 Differential absorbance of pre- and post-chlorinated porewater samples. UV refers to ultraviolet light and λ refers to wavelength.

$$\boldsymbol{\Delta UV_\lambda = UV_\lambda{}^{chlorinated} - UV_\lambda \lambda^{initial}}$$

3.7.7 Coagulation

The coagulation method used was provided by Yorkshire Water (by Jenny Banks; Technical Specialist) as the procedure typically followed their jar-test analysis for acidic waters and was used on mesocosm porewaters. Iron (III) sulphate (4 g; Sigma Aldrich, 97 % purity) was added to 500 mL ultrapure water to give a concentration of 1 g Fe L^{-1} and was used as coagulant. Raw sample was diluted 1:10 with ultra-pure water to make 50 mL of sample solution. Subsequently, 0.2 mL of coagulant was added to give a coagulant dose of 4 mg L^{-1} and samples were stirred at 100 rpm and adjusted to pH 6.1 using 0.1 M sodium hydroxide solution. Once at the correct pH, samples were stirred at 200 rpm for 30 seconds. For a further 15 minutes, samples were gently stirred at ~ 15 rpm and left to settle for 15 minutes.

The samples in this study did not coagulate following this method and did not coagulate after leaving for 7 days and stirring gently daily. The procedure was therefore repeated with 2 mL of coagulant added to each sample to give a coagulant dose of 40 mg L^{-1}, which was substantially higher than concentrations normally used with DWTPs. Samples were left for 2 weeks and were stirred daily (where time permitted) by which time, coagulation had taken place.

Samples were then filtered using 0.60 µm rhizon filters (as detailed in Section 3.3.4) and the coagulated sediment was separated from sample solution. This solution was then analysed for DOC concentration (Section 3.3.3.1) and was subsequently chlorinated (Section 7.2.4) and analysed for THM concentration (Section 7.2.3).

3.7.8 High performance liquid chromatography (HPLC)

Porewaters with sufficient sample volume following THM analysis were analysed by HPLC for DOC characterisation. An Aglient 1260 Infinity II HPLC with variable wavelength detector with an Agilent Zorbax Eclipse plus C18 (4.6 x 100 mm, 3.5 µm particle size) column, fitted with a Phenomenex SecurityGuard (C18 4.0 x 3 mm). Solvent A was water + 0.1 % formic acid and solvent B was methanol + 0.1 % formic acid (HPLC grade). The flow rate was 0.45 mL min^{-1} at 40°C. The solvent gradient was 0 min = 95 % solvent A, 5 % solvent B; 15 min = 0 % solvent A, 100 % solvent B where it was held for a further 10 min (total run time = 25 min). Injection volume was 10 µL and UV detection was at 254 nm.

3.7.9 Fourier transform infrared spectroscopy (FTIR)

Porewater samples which had undergone coagulation were analysed using FTIR for DOC characterisation. Samples and coagulant were dried at 105 °C in 30 mL crucibles for 48 hours with the residue being analysed using the method as detailed in Artz *et al* (2008). Spectra were acquired by averaging 200 scans at 4 cm^{-1} resolution over the range 4000-350 cm^{-1}. Minor variation in the amplitude between runs were corrected using a baseline. Spectra were analysed using OPUS Software (Version 7.5, build 7,5,18 (201440810)). Spectra were corrected for CO_2 and water attenuation prior to selection of peaks based upon Table 7.7 (adapted from Artz *et al*., 2008) and peak area determined. Where appropriate, peak boundaries (i.e., start and end wavelengths) were adjusted based on variation in peaks in individual samples.

3.8 Data processing and statistical analysis

All data was initially processed using Microsoft Excel (Version 2305) and pivot tables were used for initial data exploration and descriptive statistical analysis. Statistical analysis was undertaken using R Studio (Version 2021.09.0). Prior to any statistical testing, data distribution was tested for normality and the appropriate statistical test was used. Any specific statistical analysis is detailed within the results section of each chapter.

4 Effects of management on grouse-moor blanket bog soil parameters and carbon dynamics

4.1 Chapter Summary

Blanket bog is routinely burnt with the aim of managing heather growth for the benefit of red grouse populations which feature in game shoots. The impacts of heather burning upon blanket bog water quality and GHG fluxes have been extensively studied, however, findings are contradictory and there is still no consensus on the effects of burning on UK blanket bog. This study therefore aimed to assess the impacts of blanket bog management on water quality and GHG fluxes using mesocosm soil cores. Through seasonal porewater sampling, water quality in managed cores was shown to be higher than those under nil-management likely due to root exudate C input, but there was no overall difference between burnt and mown cores. The impacts of management on net C uptake was unclear but higher ecosystem respiration flux was seen in cores dominated by brash and heather, which were typically cores from unmanaged plots. Measurements from mesocosm cores were shown to be comparable to in-situ measurements for all parameters but methane fluxes suggesting meaningful comparisons can be made between mesocosms and in-situ field data. Mowing may be an alternative management regime on drier sites to improve water quality, however, depending on site and climatic conditions, this may be associated with higher methane fluxes.

4.2 Introduction

Prescribed burning of vegetation is a management regime practiced worldwide (Douglas *et al*., 2015), and in the UK, blanket bog has been routinely burnt with the aim of managing *Calluna vulgaris* (ling heather; henceforth referred to as *C. vulgaris*) growth for the benefit of red grouse (Ludwig *et al*., 2018). There are a considerable number of published studies which investigated the impacts of burning (some coupled with effects of grazing) upon water quality (e.g., Worrall, *et al*., 2007; Clay *et al*., 2009, 2010; Clay *et al*., 2012) and GHG emissions (e.g., Heinemeyer *et al*., 2023) in blanket bog draining catchments. However, findings are not unanimous and the evidence on impacts is far from clear (e.g. Harper *et al*., 2018). In addition, there has been limited work into the potential use of alternative management methods (specifically mowing – see Worrall, Rowson and Dixon, 2013), and whether this offers a suitable alternative to the management of *C. vulgaris* for grouse with regards to water quality and C dynamics. In addition, studies differ in the spatial (i.e., plot vs catchment) and temporal (i.e., few years to decades) scales investigated, as well as in their experimental design strategies, and therefore direct comparison of results is difficult.

Therefore, the aims of this work were to assess the impacts of *C. vulgaris* management (burning vs mowing vs nil heather management (henceforth referred to as uncut)) with regards to water quality parameters and GHG soil and vegetation emissions. This will contribute to the understanding of how blanket bog management impacts C dynamics and thus ES delivery. Impacts of management on a plot scale will be compared to a catchment-scale experiment (mesocosm vs in-field measurements) over seasonal and longer-term time scales.

The overarching research question for this chapter is '*Can blanket bog vegetation be managed to improve water quality, C sequestration, and GHG emissions?*'. Hypotheses tested were as follows:

I. Compared to vegetation burning, mowing management:
   a) benefits water quality via increased peat wetness,
   b) but brash decomposition alters peat chemistry and C-cycling.

II. Burning results in:
   a) greater C storage due to charcoal bypassing decomposition and negative priming of peat decomposition,
   b) but deteriorating water quality due to poly-aromatic carbohydrate inputs.

III. Vegetation, hydrology, and temperature are the main drivers affecting water quality and treatment.

4.3 Results

4.3.1 Climate comparison

The climate at the mesocosm site was on average warmer and drier than at the field sites (Table 4.1). Mean air temperature and rainfall at Heslington East for 2019-2022 was 10.38 ± 0.38 °C and 567 ± 28.60 mm compared to 7.83 ± 0.33 °C and 1665 ± 272.51 mm over the same period (Figure 4.1a and b).

Table 4.1 Mean photosynthetic active radiation (PAR), soil temperature (T_{soil}) and air temperature (T_{air}), and total annual rainfall for the Heslington East (York) mesocosm site and field sites (two blanket bogs in the Yorkshire Dales and one in Lancashire).

Year	PAR (mol yr^{-1})	T_{soil} (°C)	T_{air} (°C)	Rainfall (mm)
Heslington East				
2019	6543	10.3	10.1	540
2020	7063	10.5	10.4	551
2021	6953	10.4	10.1	572
2022	7382	11.11	10.9	605
Nidderdale, Mossdale, and Whitendale				
2019	6689	8.0	7.6	1809
2020	6889	8.0	4.8	1975
2021	7179	7.9	7.6	1476
2022	7116	8.5	8.3	1400

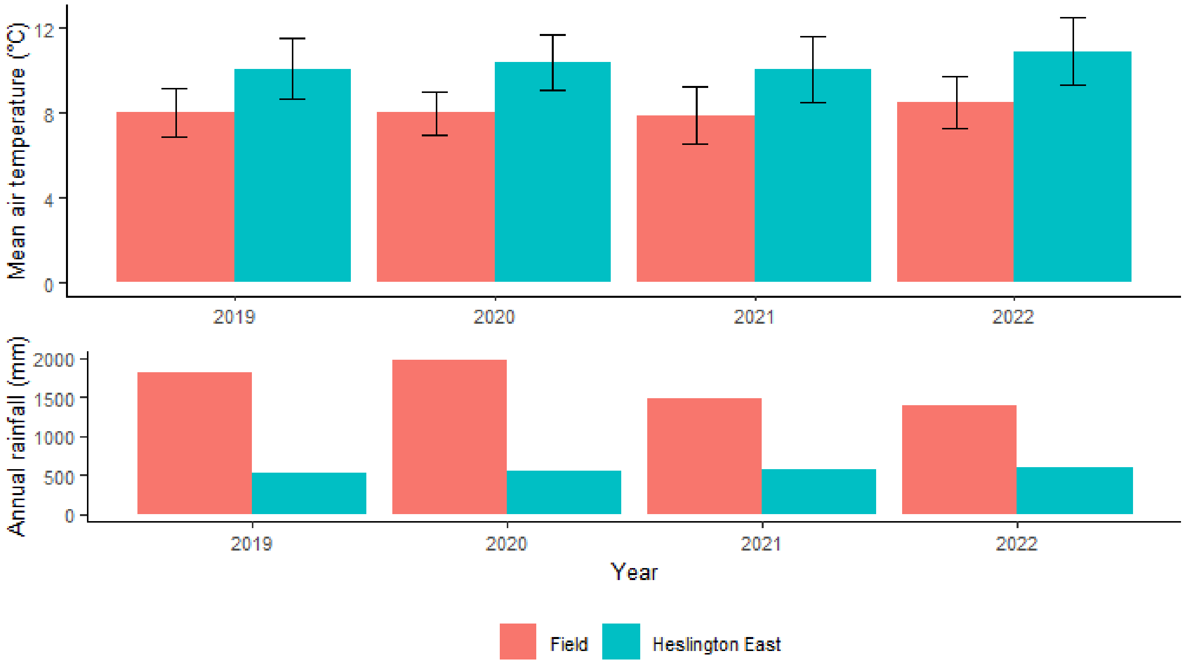


Figure 4.1 Mean air temperature (A) and total annual rainfall (mm) for the field sites (Nidderdale, Mossdale, and Whitendale) and mesocosm (Heslington East, York) sites.

4.3.2 Water table depth

WTD was comparable between the mesocosms and field sites. In 2019, WTD was maintained at -5 cm below surface, whilst in 2020-2022, the aim was to maintain it to field conditions. The mean WTD of mesocosm cores was -9.40 ± 3.28 compared to -12.02 ± 3.17 of field plots (Table 4.2).

Table 4.2 Mean water table depth of mesocosms and *in situ* field plots. In-situ measurements were measured manually whilst mesocosm water table depth was measured via a logger.

Management	Mean water table depth (cm) ± standard deviation
Mesocosm	
Burnt	-9.08 ± 3.48
Mown	-9.58 ± 3.56
Uncut	-9.51 ± 3.49
In-field	
Burnt	-11.18 ± 3.29
Mown	-11.49 ± 2.79
Uncut	-13.40 ± 3.29

4.3.3 Vegetation

A non-metric multidimensional scaling technique (NMDS) (R package "vegan", Oksanen *et al.*, 2022) (Figure 4.2) was performed on annual mesocosm vegetation survey data (stress = 0.23) showing vegetation coverage (%) differed significantly between site and management regime (ANOSIM R stat = 0.18 and 0.13 and RMSE = 0.00001 with 9.9 K dimensions respectively). Indicator species analysis (R package "indicspecies", Cáceres *et al.*, 2022) identified species most associated with management regime (Table 4.3). Of note is that *Sphagnum* and *C. vulgaris* was most associated with uncut plots, whilst burnt plots were most associated with shrubs, and mown plots with sedge. *% C. vulgaris* coverage was shown to be significantly higher on uncut cores compared to mown cores (ANOVA, F = 4.759, *df* = 2, p = 0.009; Tukey HSD, p = 0.007).

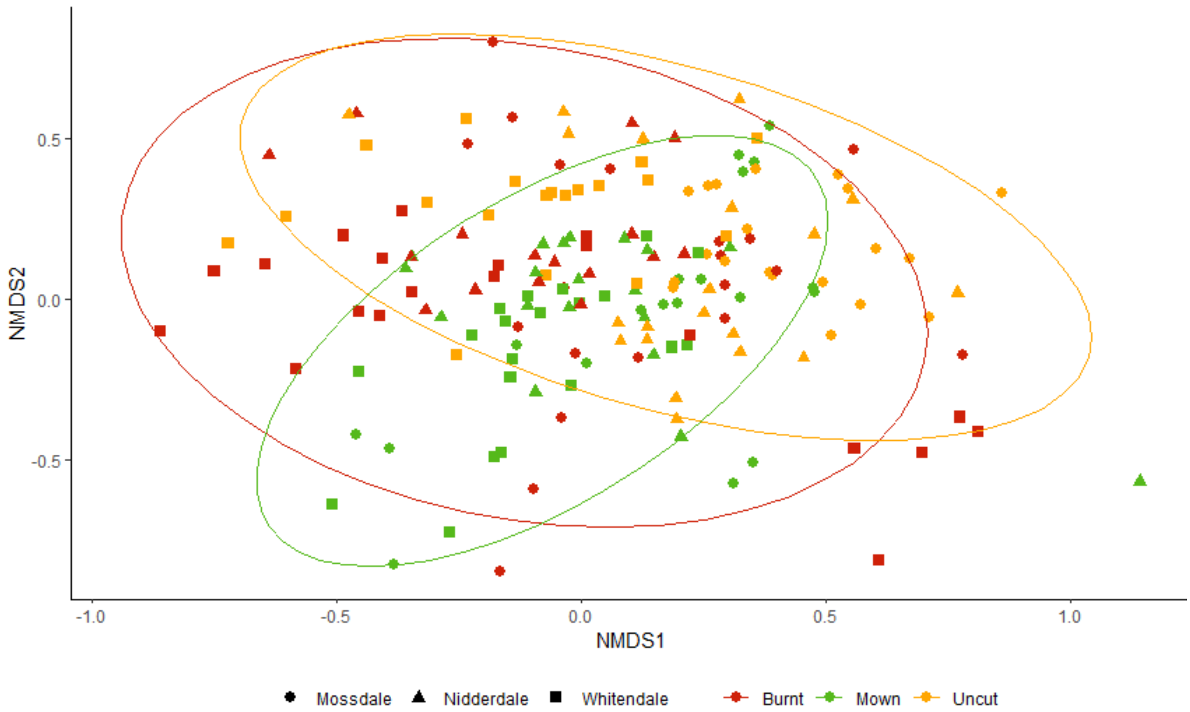


Figure 4.2 A non-metric multidimensional scaling technique (NMDS) of vegetation groups of mesocosm central cores for the three grouse moors (Nidderdale, Mossdale, and Whitendale) in the Yorkshire Dales and Forest of Bowland under three management regimes (burnt, mown, and 'uncut' (nil heather management)). Ellipses show NMDS based grouping of mesocosm cores of the same management.

Table 4.3 Indicator species analysis based on the total % vegetation cover of the mesocosm cores (using R stats package "indicspecies", Cáceres *et al*., 2022) showing key vegetation groups significantly associated ($p < 0.05$) with each management (burnt, mown and uncut (nil heather management)) regime. Number of iterations = 9999.

	Stat	P value
Burnt		
Shrub	0.34	< 0.001
Herb	0.17	0.013
Other moss	0.17	0.005
Mown		
Sedge	0.43	< 0.001
Uncut		
Brash	0.37	< 0.001
Sphagnum spp.	0.22	< 0.001
C. vulgaris	0.15	0.015

Vegetation groups significantly associated with each site are shown in Table 4.4. *Sphagnum spp*. were significantly associated with Mossdale (generally the wettest site and of the three and the site considered to be the most 'intact' (Heinemeyer *et al*., 2019)). ANOVA suggested that *C. vulgaris* differed between site (ANOVA, F = 10.49, df = 2, $p < 0.001$), with Whitendale having significantly higher % coverage than Nidderdale and Mossdale (Tukey HSD, $p < 0.001$). However, it is likely that the high % coverage on Whitendale uncut cores skewed this result (Figure 4.3).

At the site level, *Sphagnum* coverage was significantly higher on uncut cores for Nidderdale and Mossdale, whilst at Whitendale, burnt cores had the highest mean coverage. However, this was skewed by one core (WF4; 64.4%). Brash coverage was consistently highest for uncut cores from all sites and was significantly higher compared to the other management regimes at Nidderdale and Mossdale (ANOVA, $p < 0.05$). Median sedge coverage was highest on mown cores at all sites but was only significantly higher on cores from Mossdale and Whitendale (all statistical test results shown in Figure 4.3).

Table 4.4 Indicator species analysis (using R stats package “indicspecies”, Cáceres *et al*., 2022) results showing key vegetation groups significantly ($p < 0.05$) associated with grouse moor site (Nidderdale, Mossdale, and Whitendale). Number of iterations = 9999.

	Stat	P value
Nidderdale		
Bare	0.28	< 0.001
Herb	0.17	0.009
Brash	0.17	0.005
C. vulgaris	0.24	< 0.001
Other moss spp.	0.51	< 0.001
Mossdale		
Sphagnum spp.	0.353	0.0001
Sedge	0.251	0.0003
C. vulgaris	0.24	< 0.001
Whitendale		
Shrub	0.44	< 0.001
Other moss spp.	0.51	< 0.001

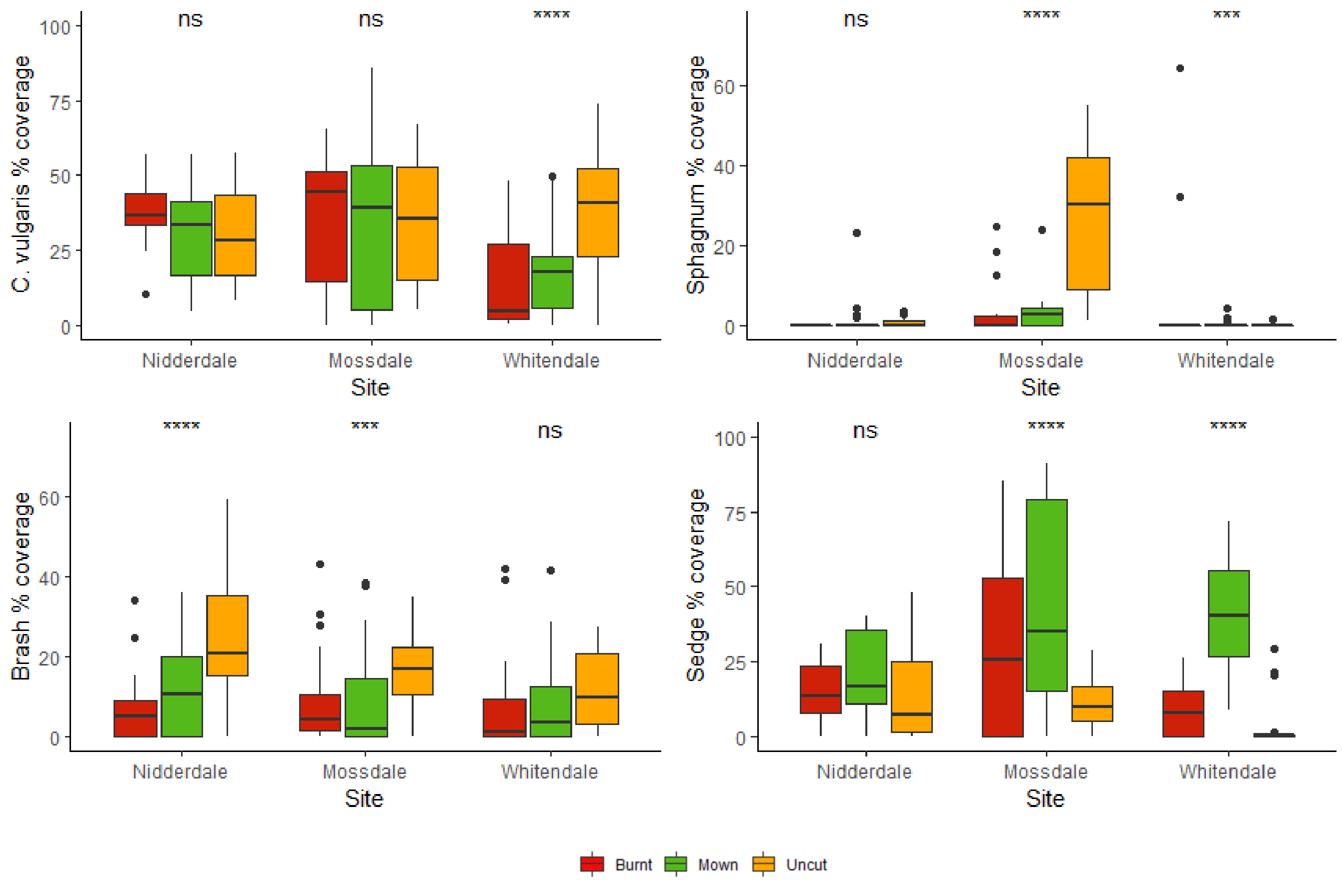


Figure 4.3 (A) *Calluna vulgaris*, (B) *Sphagnum* spp., (C) brash and (D) sedge % coverage of vegetated mesocosm cores from all three management regimes (burnt, mown, and uncut) for the three grouse moors (Nidderdale, Mossdale, and Whitendale) in the Yorkshire Dales and Lancashire. Significance testing (ANOVA) results shown. A non-significant difference is indicated by ns and a significant difference by *. * = significant p < 0.05, *** = very significant p < 0.01, **** = extremely significant p < 0.001. Note the axis for *Sphagnum* and brash.

4.3.4 Soil analysis

The following results refer to peat soil samples which were collected ~ 5-15 cm below the peat surface alongside the mesocosm cores in January and February 2019.

4.3.4.1 Bulk Density (BD)

BD ranged from 0.05 g cm^3 – 0.17 g cm^3 with both a median and mean of 0.10 ± 0.03 g cm^3. BD did not differ between management regime (ANOVA, F = 2.131, df = 2, p = 0.135) but differed significantly between Nidderdale and Mossdale samples (ANOVA, F = 5.83, df = 2, p = 0.007, Tukey HSD, p = 0.004). Nidderdale had the highest mean BD whilst Mossdale had the lowest (0.12 ± 0.02 g cm3 compared to 0.08 ± 0.02 g cm3). At all sites, burnt samples had a higher BD than the other management regimes (Figure 4.4).

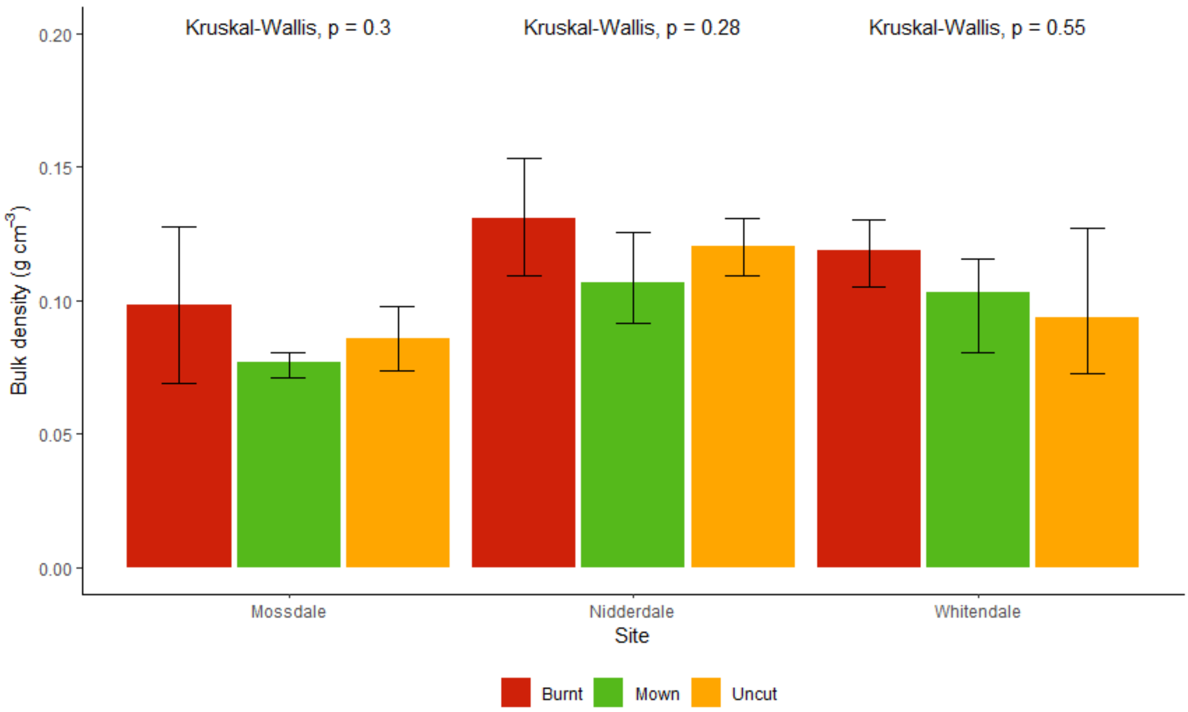


Figure 4.4 Mean bulk density of peat soil samples taken alongside the mesocosm cores. Error bars represent standard deviation. N = 36, n = 4 per management regime (burnt, mown, and uncut) per site (Nidderdale, Mossdale, and Whitendale).

4.3.4.2 Soil moisture

Soil moisture (SM) in the peat samples collected alongside the mesocosm cores ranged from 70.7 - 93.4 % with a median of 86.8 ± 3.1 % and a mean of 86.7 ± 3.9 %. At each site, samples from mown plots had higher SM than burnt plots; however, this difference was not significant (KW chi-squared = 3.65, df = 2, p = 0.161; Figure 4.5). SM differed significantly between site (KW chi-squared = 11.11, df = 2, p = 0.004) with Mossdale being significantly wetter than Nidderdale and Whitendale (Pairwise Wilcoxon post-hoc, p = 0.002 and p = 0.03 respectively). However, this was only a 5 % and 3 % difference respectively. BD and SM were significantly negatively correlated (p < 0.001; see Figure 4.6) as expected.

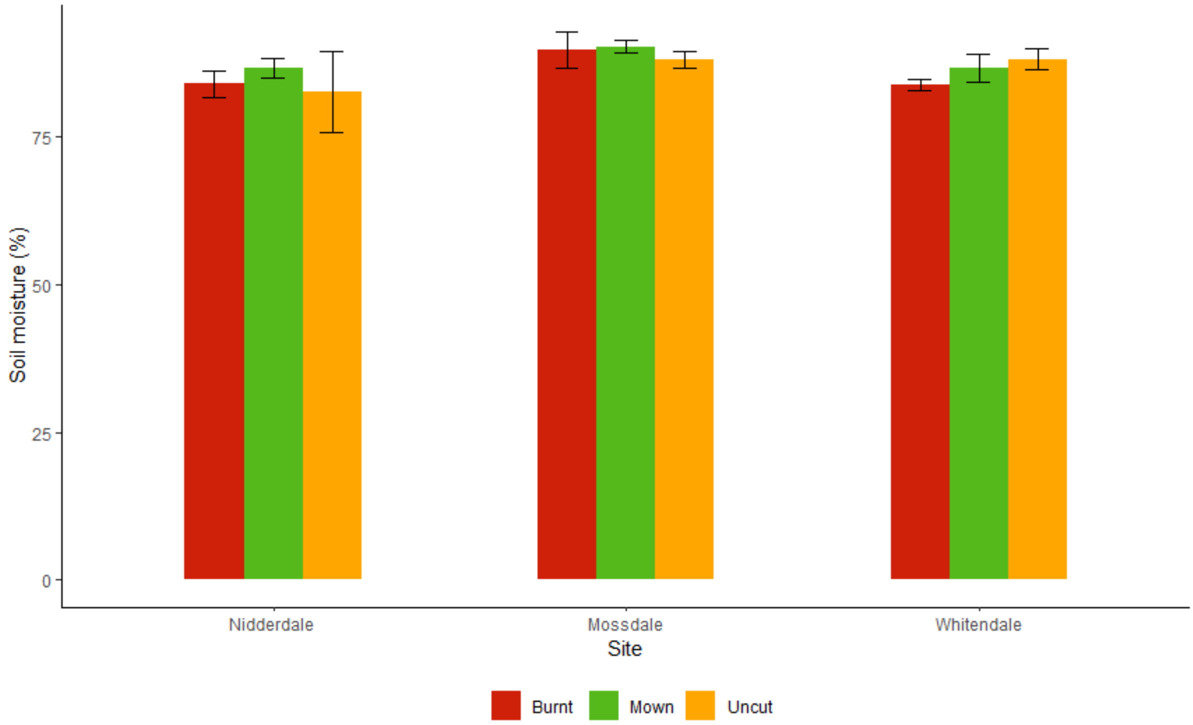


Figure 4.5 Soil moisture of peat soil samples taken ~5-15 cm below the peat surface from the three managed grouse moor blanket bog sites (Nidderdale, Mossdale and Whitendale). Burnt, mown and uncut refer to management regime. N = 36, n = 4 for each management regime at each site. Error bars represent standard deviation. 100 % soil moisture equals saturation.

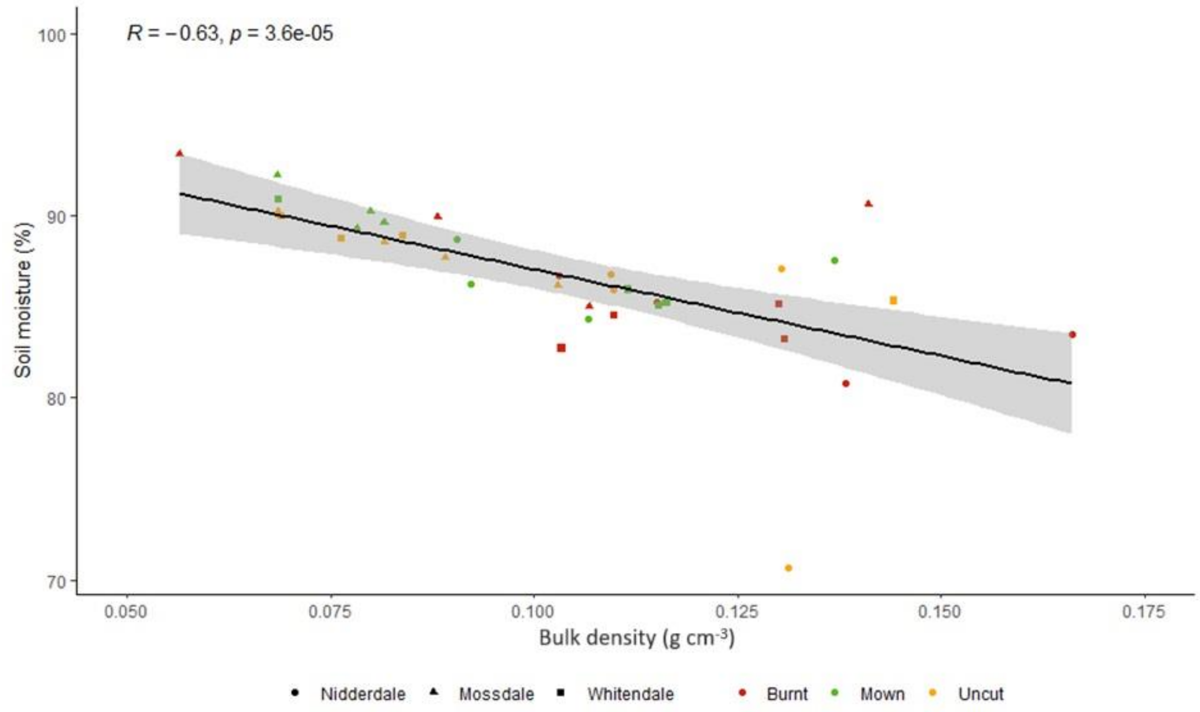


Figure 4.6 Correlation between bulk density (g cm^{-3}) and soil moisture (%) of peat samples taken 5-15 cm below the peat surface from the three managed grouse moor sites (Nidderdale, Mossdale, and Whitendale). The linear regression line of best fit is shown in black with shaded areas indicating the 95% confidence interval.

4.3.4.3 Percentage organic soil carbon (% C_{org})

The % C_{org} of peat soil ranged from 41.6 – 52.7 % with a median of 50.5 ± 1.7 % and a mean of 49.1 ± 8.2 %. Figure 4.7 shows site and management comparisons. Mown plots had significantly lower median % C_{org} at each site compared to uncut and burnt plots (KW chi-squared = 11.35, df = 2, p = 0.003, Pairwise Wilcoxon p = 0.009 and p = 0.01 respectively) and Nidderdale differed from Mossdale (KW chi-squared = 7.22, df = 2, p = 0.02, Pairwise Wilcoxon p = 0.049), however this was only by 3%.

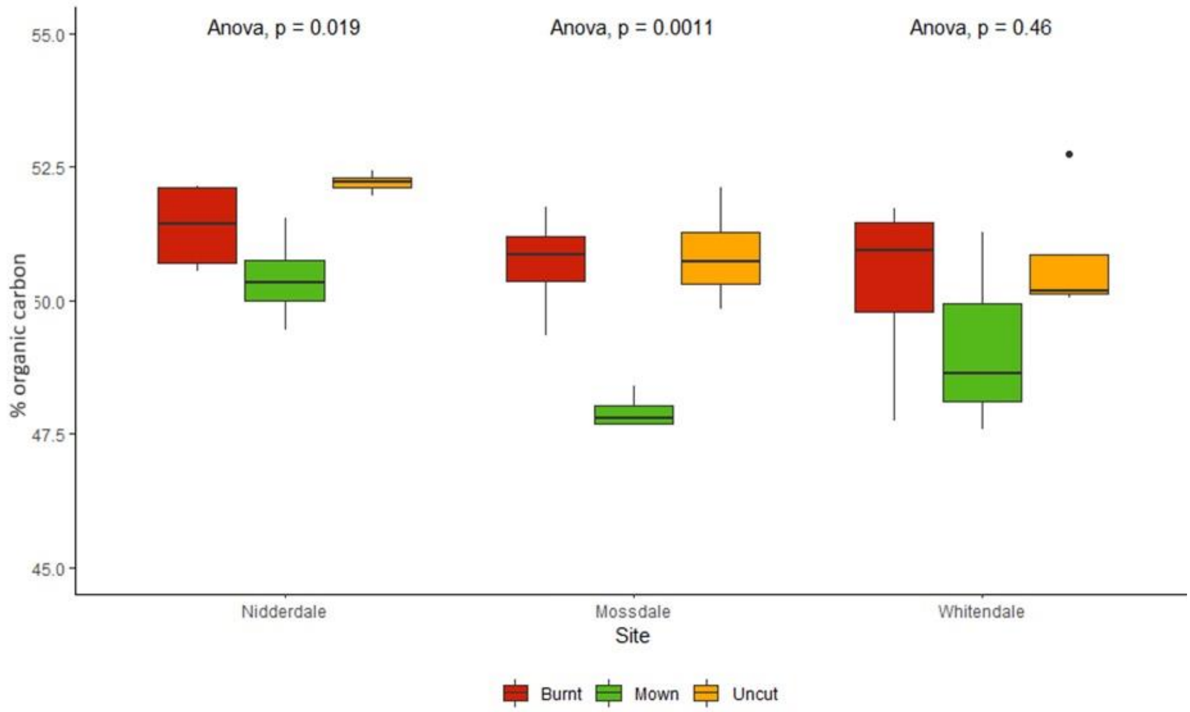


Figure 4.7 % organic carbon (% C_{org}) of peat soil samples taken ~5-15 cm below the peat surface from three grouse-managed blanket bog (Nidderdale, Mossdale, and Whitendale) under three management regimes (burning, mowing, and uncut). Note the y-axis range. Significance testing results shown.

4.3.4.4 C:N ratio

C:N of peat soil ranged from 16.72 – 83.84 with a median of 29.70 ± 7.60 and a mean of 31.05 ± 10.98. C:N of samples taken from Whitendale are significantly lower than those from Nidderdale and Mossdale (KW chi squared = 14.72, df = 2, p = 0.0006; Pairwise Wilcoxon, p = 0.006 and p = 0.0006 respectively). Burnt samples had the lowest C:N from both Nidderdale and Mossdale; however, this difference was not significant (KW chi-squared = 0.66, df = 2, p = 0.72).

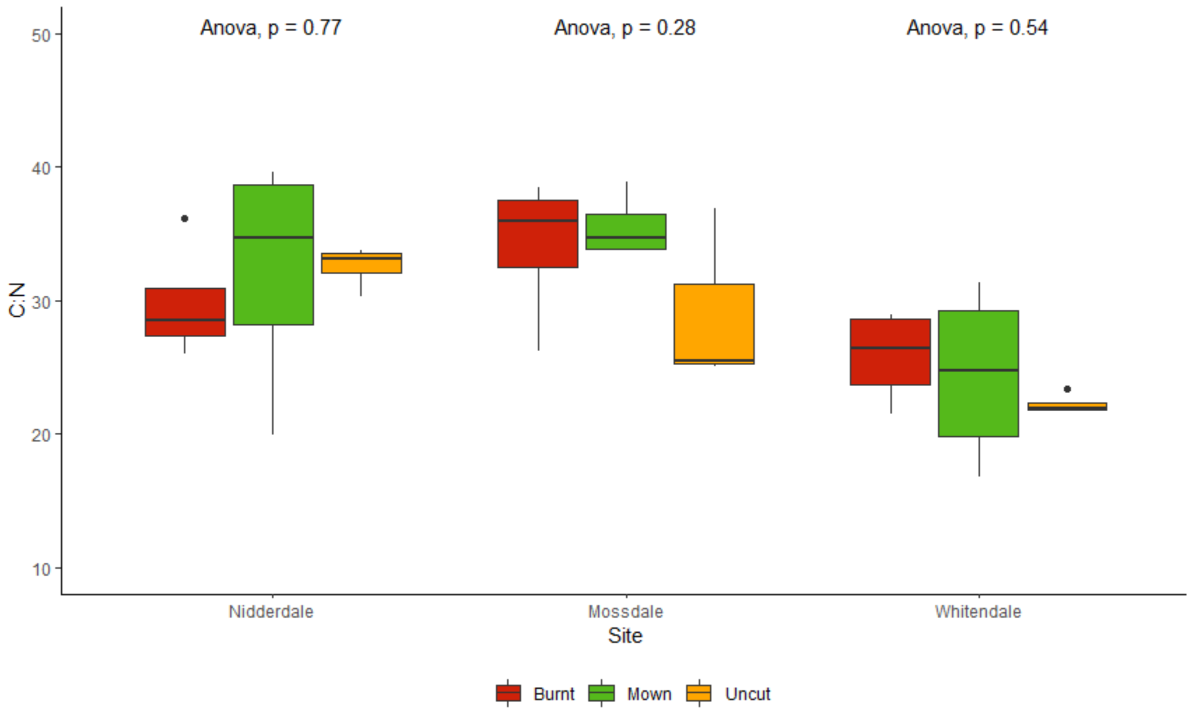


Figure 4.8 C:N for peat soils samples from managed grouse blanket bog ~5-15 cm below the peat surface. Nidderdale, Mossdale and Whitendale refer to the site whilst burnt, mown and uncut (no heather management) refer to management regime. Statistical testing results shown.

4.3.4.5 Linking soil parameters to environmental conditions and management and site

A NMDS was performed to determine if there was an association between site or management regime and soil properties (including but not limited to % C_{org}, C:N, and BD), and to determine likely drivers of differences in soil property parameters. Management regime and site were used to centre the scores for the NMDS, and environmental parameters were used as vectors (Table 4.5). Latitude was removed as this did not differ between sites. Soil properties were shown to not differ significantly between management regime (ANOSIM R stat = -0.02, p = 0.70, permutations = 9999) but did differ significantly between site (ANOSIM R stat = 0.27, p < 0.01, permutations = 9999) as also shown by the NMDS elipitical groupings (Figure 4.9).

Elevation was shown to be the only likely significant driver (Table 4.6) and caused skew along NMDS1 for Nidderdale cores. Nidderdale uncut cores were at the highest elevation of all core collection locations, but these were not at a significantly higher elevation compared to Whitendale.

Table 4.5 Centroids of factors (grouse moor site and management (burning, mowing and uncut)) for non-metric multidimensional scaling analysis.

		NMDS1	NMDS2
Site	Nidderdale	-0.0319	-0.0128
	Mossdale	-0.0571	-0.0058
	Whitendale	-0.0252	0.0186
Management	Burnt	-0.0062	-0.0116
	Mown	0.0195	-0.0120
	Uncut	-0.0134	0.0236
Goodness of fit			
	R^2	**Pr (>r)**	
Site	0.37	**0.001**	
Treatment	0.10	0.142	

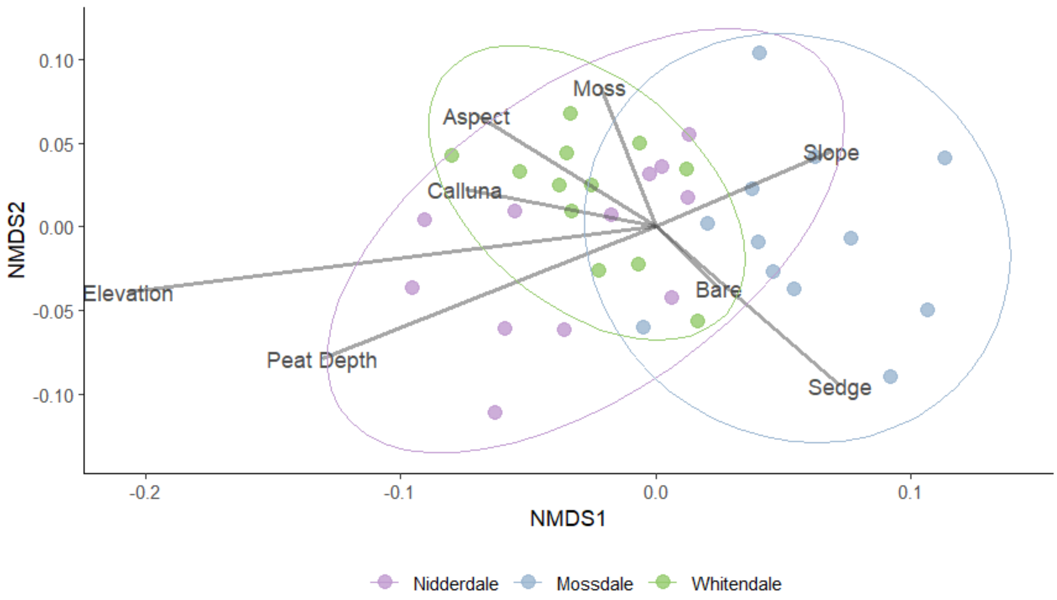


Figure 4.9 Non-metric multidimensional scaling of vegetation groups and environmental factors linked to soil quality parameters (see Table 4.7) from three grouse-managed blanket bog sites (Nidderdale, Mossdale, and Whitendale). Ellipse show grouping of cores taken from the same site.

Table 4.6 Non-metric multidimensional scaling (NMDS), R^2, and probability scores for vectors used in NMDS analysis for the factors influencing soil quality parameters (bulk density, % organic carbon, carbon:nitrogen, and soil moisture). Parameters with significant p values are indicated in **bold**. *Sphagnum* had an R^2 of 0 and was therefore removed.

Environmental factor	NMDS1	NMDS2	R^2	Pr (>r)
Calluna vulgaris	-0.96	0.29	0.04	0.50
Moss	-0.25	0.97	0.05	0.41
Sedge	0.61	-0.80	0.09	0.20
Bare ground	0.56	-0.83	0.13	0.80
Slope	0.84	0.55	0.05	0.47
Aspect	-0.72	0.69	0.06	0.34
Elevation	-0.98	-0.18	0.29	**0.003**
Peat Depth	-0.85	0.52	0.15	0.06

A summary of the significant differences in soil parameters presented thus far between site, management, and management differences at a site level for key soil parameters is shown in Table 4.7. .

Table 4.7 P values from statistical analysis of soil variables (bulk density (g cm^{-3}), soil moisture (%), % organic carbon (% C_{org}), and carbon: nitrogen (C:N) of managed blanket bog. Significant differences (P < 0.05) are indicated in bold. . Bulk density was normally distributed and therefore analysed using ANOVA whilst soil moisture, % C_{org}, and C:N were non-normally distributed and could not be transformed to achieve normality, so were therefore analysed using the Kruskal Wallis significance test.

	Bulk density (g cm^{-3})		Soil moisture (%)		% C_{org}		C:N	
	F	***p***	**χ^2**	***p***	**χ^2**	***p***	χ2	p
Site	5.83	**0.007**	11.11	**0.004**	7.22	**0.03**	14.72	**<0.001**
Management	2.131	0.135	3.65	0.161	11.354	**0.003**	0.66	0.71
Site * management	0.290	0.88	-	-	-	-	-	-

4.3.5 Water quality

This section details results of water quality analysis undertaken on mesocosm porewater samples collected July 2019 – November 2022.

4.3.5.1 Dissolved organic carbon

Vegetated core mesocosm pore water DOC concentration ranged from 2.95 mg L^{-1} to 397.98 mg L^{-1} with a median of 72.97 mg L^{-1} and a mean of 80.98 ± 46.77 mg L^{-1} (standard deviation) (Table 4.8).

Table 4.8 Descriptive statistics for DOC concentration (mg L^{-1}) of mesocosm central vegetated core pore water from three grouse managed (burnt, mown, uncut) blanket bog sites (Nidderdale, Mossdale, and Whitendale). SD refers to standard deviation. Number of samples varies per site and treatment due to insufficient water sample collected on some dates.

	Minimum	Maximum	Median	Mean	SD	*n =*
All	2.95	397.98	72.97	80.98	46.77	351
Burnt	15.76	226.94	74.24	80.06	43.33	119
Mown	18.50	397.98	66.28	74.72	48.13	115
Uncut	2.95	258.55	78.83	88.05	47.62	117
Nidderdale	13.01	226.94	76.33	84.72	41.62	117
Mossdale	2.95	397.98	59.71	74.36	55.05	115
Whitendale	17.50	211.75	78.31	83.69	41.70	119

Mossdale samples had the lowest median DOC concentration of 59.71 mg L^{-1} and Nidderdale had the highest median DOC concentration of 78.31 mg L^{-1} (Figure 3a), yet this difference was not significant (ANOVA, F = 1.734, df = 2, p = 0.18). However, prior to the additional November 2022 collection, this difference was significant (ANOVA, F=7.63, df = 2, p = 0.0006) with Mossdale DOC concentration being significantly lower than for Nidderdale and Whitendale (post-hoc Tukey p = 0.001 and 0.004, respectively). The mean DOC concentration of samples collected in November 2022 was 130.41 ± 74.51 mg L^{-1}, which was higher than the mean DOC concentration of samples collected the previous year (103.64 ± 39.35 mg L^{-1}) but not significantly different (KW chi squared = 1.32, df = 1, p = 0.25). Mossdale DOC concentration was significantly higher than Nidderdale and Whitendale in November

2022 (Figure 4.10 C), increasing overall site median DOC concentration, thus masking site differences. During the summer of 2022, there was a prolonged drought period with elevated temperatures, and thus there were periods of drying and rewetting. Of the three grouse moor managed sites, in-situ peat soil moisture over the study period was highest at Mossdale, and the site received the highest rainfall (annual precipitation 2029 mm compared to 1587 mm and 1858 mm for Nidderdale and Whitendale respectively for 2014-2019; Heinemeyer *et al*., 2019). % C_{org} of peat soil was lowest for Mossdale samples and was significantly lower than %C of Nidderdale (Kruskal Wallis chi-squared = 6.55, df = 2, p = 0.038, pairwise Wilcoxon p = 0.05). However, the mean % C difference was only 1.5%.

DOC concentration did not differ significantly between management regime (ANOVA, F=2.409, df = 2, p = 0.09, Figure 4.10 b). Median DOC concentration was highest in uncut cores and lowest in mown cores (78.84 mg L^{-1} compared to 66.28 mg L^{-1}) with burnt cores showing intermediate median DOC concentration overall (66.28 mg L^{-1}) Uncut cores had a higher median *C. vulgaris* coverage than burnt and mown cores (median % coverage of 33.1 ± 18.5 % compared to 28.6 ± 19.5 % and 25.3 ± 19.9 % respectively, whilst ANOVA F=4.76, df = 2, p = 0.009; post-hoc Tukey indicated uncut had a significantly higher *C. vulgaris* coverage than mown cores, p = 0.007). However, there was no correlation between *C. vulgaris* coverage and DOC concentration (R = 0.08, p = 0.02, method = Pearson). There was a significant correlation between DOC concentration and brash coverage (R = 0.22, p < 0.01, method = Pearson) and a significantly higher brash coverage on uncut mesocosms compared to burnt and mown cores (ANOVA, F = 29, df = 2, p < 0.001, post-hoc Tukey p < 0.001). At the site level, there were only differences between managements at Whitendale (ANOVA, F=, df = 2, p = 0.019; Figure 4.10), with uncut cores having significantly higher DOC concentration than burnt and mown cores.

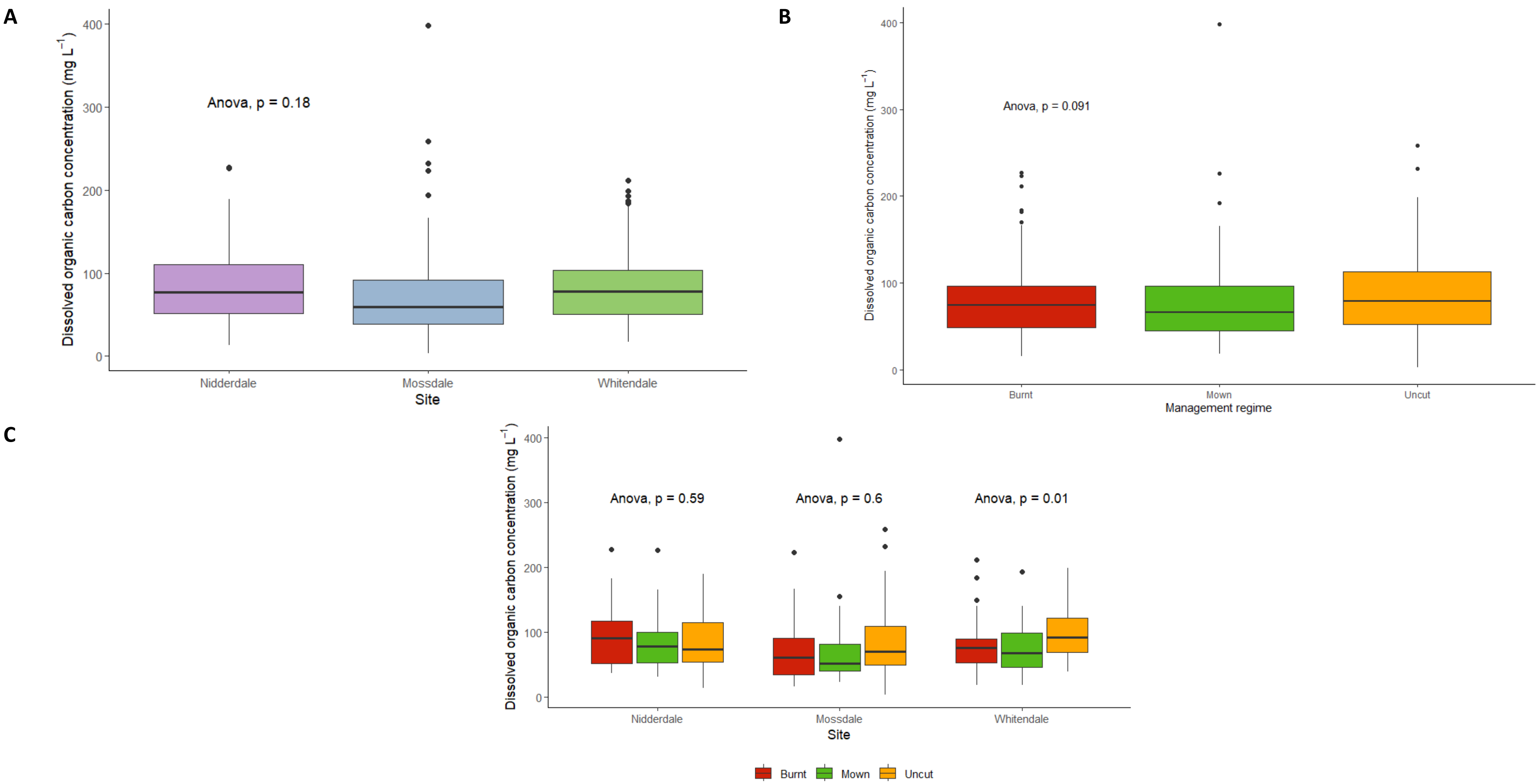


Figure 4.10 Dissolved organic carbon concentrations of mesocosm pore waters from three blanket bog sites (Nidderdale, Mossdale, and Whitendale). Boxes represent the second and third quartile and the median. Outliers are shown beyond the whiskers. Burnt, mown and uncut refer to the three management regimes. n = 351.

Cores were classified by dominant vegetation type, i.e., the vegetation group which has the highest % coverage on a core. The median DOC concentration for cores dominated by other moss was the highest of all dominant vegetation types (Figure 4.11); however, DOC concentration was only significantly higher than in cores dominated by brash (Tukey post-hoc, p = 0.02). DOC concentration varied significantly between cores with different dominant vegetation cover (ANOVA, F = 2.86, df = 4, p = 0.02); however, when site and treatment were accounted for, this difference was no longer significant (ANOVA, F = 0.46 and 0.76, df = 7, p = 0.84 and p = 0.62 for dominant vegetation group within the same site and management regime respectively).

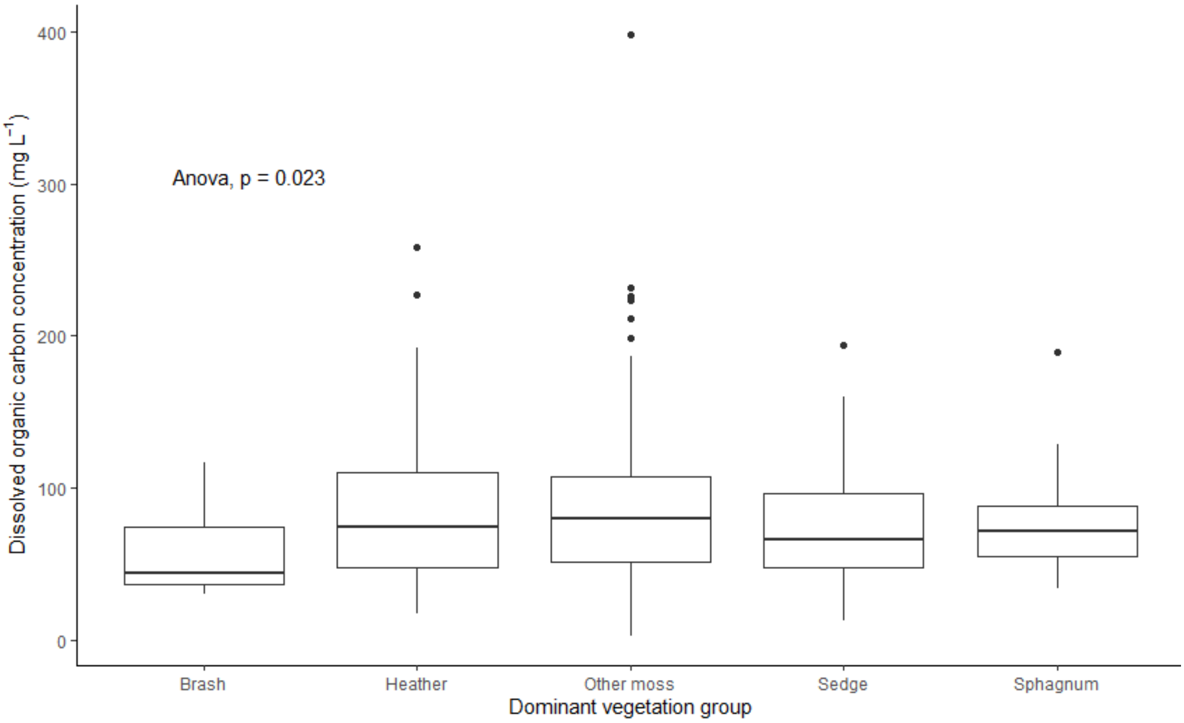
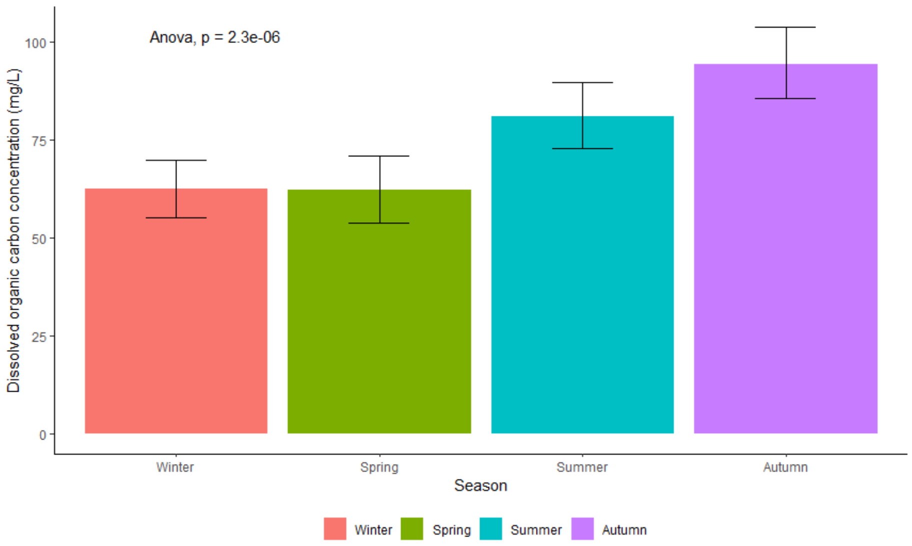


Figure 4.11 Dissolved organic carbon concentration (mg L^{-1}) of mesocosm pore waters from three blanket bog sites (Nidderdale, Mossdale, and Whitendale) and core dominant vegetation type. Significance testing result displayed.

4.3.5.2 Seasonal variation in dissolved organic carbon concentration

Sample collection dates were categorised into seasons: winter included collections from December, January, and February; spring from March, April, and May; summer from June, July, and August; and autumn from September, October, and November. Mean DOC concentration was highest in autumn overall and for all treatments (Figure 4.12 A and B) and was shown to differ significantly between seasons (ANOVA, F = 10.06, df = 3, p < 0.001) with post-hoc Tukey testing showing spring-autumn (p < 0.01), winter-autumn (p < 0.001) and winter-summer (p = 0.04) being significantly different. On a seasonal basis, uncut cores consistently had a higher mean DOC concentration compared to burnt and mown cores.

A



B

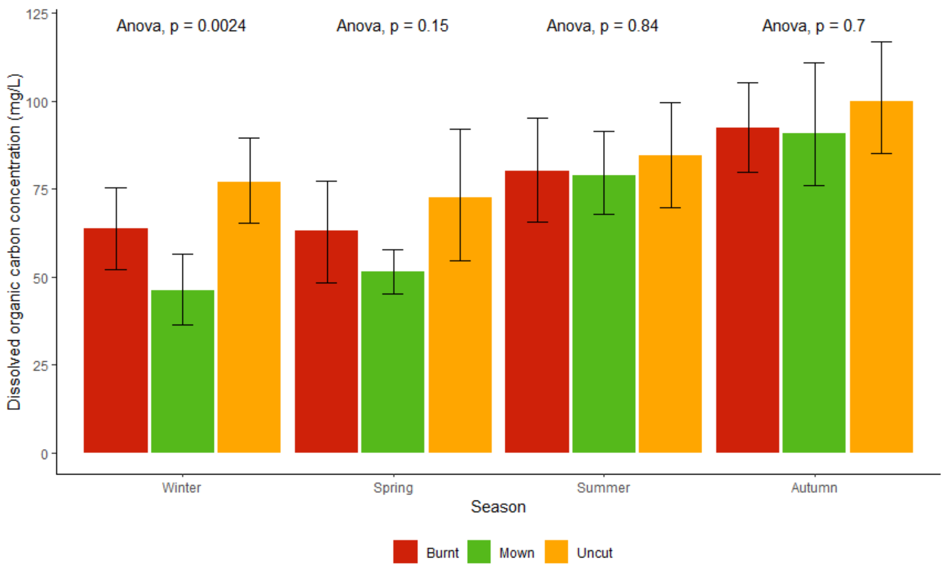


Figure 4.12 **A**) Seasonal (winter = December, January, and February, spring = March, April, and May, summer = June, July, and August, and autumn = September, October, and November) mean dissolved organic carbon (DOC) concentration for mesocosm cores from three grouse-moor blanket bog (Nidderdale, Mossdale, and Whitendale). Error bars show standard error. **B**) Seasonal mean dissolved organic carbon concentration for three grouse-moor blanket bog under three management regimes (burnt, mown and uncut). Error bars show standard error. Statistical testing results displayed.

4.3.5.3 *Drivers of DOC concentration*

Environmental variables which may be driving DOC concentrations were centered and Z-scored prior to plotting a correlation matrix using the R package "corrplot" (Wei & Simko, 2017). The variables significantly correlated for DOC concentration are listed in Table 4.9.

Table 4.9 Environmental variables significantly correlated with mesocosm pore water dissolved organic carbon concentration in cores from managed (burnt, mown, and uncut plots).

Correlated environmental variables	R value	P value
Water table depth (cm)	-0.26	< 0.001
Air temperature (°C)	0.28	< 0.001
pH	-0.15	0.006
Conductivity	0.38	< 0.001
% *Calluna vulgaris* cover	0.12	0.024
% sedge cover	-0.14	0.006
% *Sphagnum* spp. cover	-0.11	0.04
% brash cover	0.22	< 0.001

Relationships between DOC concentration and environmental variables (listed in Table 4.9) were assessed using a generalised linear model (GLM) as DOC concentration was approaching a normal distribution and was continuous and unbounded. To address issues of multi-collinearity, variables (soil temperature, light levels, and soil moisture) were removed from the dataset based upon their hypothesised relevance to water quality parameters (e.g., Artz *et al*., 2013). Latitude and longitude of core collection sites were removed as they were no longer a representation of the climatic conditions which the peat cores were under. Multi-collinearity was assessed though variance inflation factors (VIF) using the "car" R package (Fox & Weisberg, 2019). The initial model run showed VIF values < 2 for all variables other than conductivity and pH which were removed. The second model run obtained VIF values of < 2 for all variables. A model was obtained using 6 variables: water table depth, air temperature, % *C. vulgaris* cover, % sedge cover, % *Sphagnum* spp. cover, and % brash cover. Air temperature, % *Sphagnum* spp, and % brash cover were significant predictors of DOC (Table 4.10).

Table 4.10 Estimates, error, T, P, VIF (variance inflation value) and AIC values of a general linear model assessing the impact of environmental variables on DOC concentration.

Coefficients	**Estimate**	**Std. Error**	**T value**	***p*-value**	**VIF**	**AIC**
Intercept	101.61	10.46	9.71	< 0.001	-	2079.9
Water table depth	0.12	0.40	0.32	0.75	1.24	
Air temperature	**-2.13**	**0.81**	**-2.64**	**0.009**	**1.20**	
% C. vulgaris cover	-0.12	0.13	-0.92	0.36	1.19	
% Sedge cover	-0.16	0.12	-1.40	0.16	1.32	
% Sphagnum spp. cover	**-0.59**	**0.19**	**-3.19**	**0.002**	**1.08**	
% Brash cover	**0.50**	**0.17**	**2.89**	**0.004**	**1.09**	

4.3.5.4 Dissolved organic carbon differences between main and side cores

DOC was measured in all central vegetated cores and the two auxiliary side cores (one where roots were permitted to grow into, and the other where roots were repeatedly cut). The intention was to be able to assess if DOC fluxes differ between vegetation, root, and microbial components.

The mean DOC concentration was highest in cores void of vegetation but with roots permitted (Table 4.11); however, there was no significant difference between the three cores (ANOVA, F = 0.42, df = 2, p = 0.657) and the mean and median were comparable for all cores (Table 4.11). At the site level, were no differences between DOC concentration in the main vs side cores (ANOVA, F = 0.29, df = 2, p = 0.884 and F = 0.11, df = 2, p = 0.98 respectively; Figure 4.13).

Table 4.11 Descriptive statistics for porewater dissolved organic concentration (mg L^{-1}) for each mesocosm core: 'Main' refers to the central vegetated core; 'Roots' refers to the auxiliary side core where vegetation growth was not permitted but roots were left; and 'Cut' refers to the side core where both vegetation and root growth were not permitted.

	Min	Max	Median	Mean	SD
Main	2.946	321.66	68.25	75.70	42.78
Roots	15.76	269.42	68.65	78.31	46.59
Cut	15.50	314.09	66.28	75.50	43.32

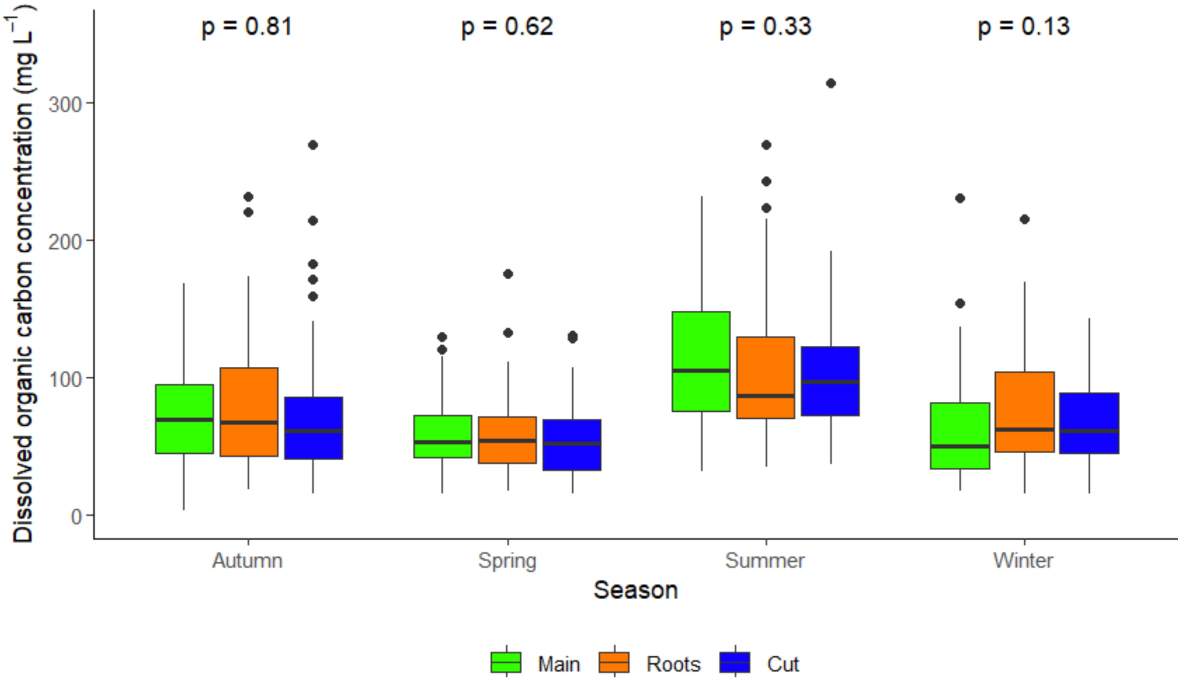


Figure 4.13 Seasonal dissolved organic carbon concentration (mg L^{-1}) of mesocosm pore waters for the three mesocosm cores - 'Main' refers to the central vegetated core, 'Roots' refers to the auxiliary side core where vegetation growth was not permitted but roots were left and 'Cut' refers to the side core where both vegetation and root growth were not permitted. n = 283 for main cores, n = 279 for cores with roots, and n = 271 for cores where no vegetation growth was permitted.

4.3.5.5 Dissolved organic nitrogen (DON)

DON ranged from 0.2 mg L^{-1} - 11.8 mg L^{-1} with a median of 2.4 mg L^{-1} ± 1.8 and a mean of 3.2 mg L^{-1} ± 2.33 (Table 4.12). DON was shown to be significantly positively correlated with DOC concentration (Pearson correlation = 0.52, $p < 0.001$, Figure 4.14).

Porewater from uncut cores had significantly higher DON compared to burnt and mown cores (ANOVA, F=12.96, df = 2, $p < 0.001$, post-hoc Tukey $p < 0.01$) with a median of 3.77 mg L^{-1} compared to 2.88 mg L^{-1} and 2.50 mg L^{-1} respectively (Table 4.12). Mossdale had significantly lower DON compared to Nidderdale and Whitendale (ANOVA, F=10.14, df = 2, $p < 0.001$, post-hoc Tukey $p < 0.01$). Within site differences were present at Mossdale and Whitendale where uncut porewater DON was significantly higher than mown and burnt samples; however, this was not seen at Nidderdale (Figure 4.15).

Table 4.12 Descriptive statistics for dissolved organic nitrogen concentration (mg L^{-1}) of mesocosm central vegetated core pore water from grouse managed blanket bog sites. SD refers to standard deviation. Number of samples varies per site and treatment due to insufficient water sample collected for analysis. * refers to a concentration below the limit of detection.

	Minimum	Maximum	Median	Mean	SD	*n* =
All	< 0.01 *	16.29	3.01	3.47	4.2	351
Burnt	< 0.01 *	16.29	2.88	3.16	2.16	119
Mown	< 0.01 *	11.90	2.50	2.86	1.71	115
Uncut	< 0.01 *	14.05	3.77	4.40	2.93	117
Nidderdale	< 0.01 *	11.90	3.47	3.67	2.23	117
Mossdale	< 0.01 *	6.29	1.93	2.65	2.17	115
Whitendale	< 0.01 *	14.05	3.61	4.06	2.59	119

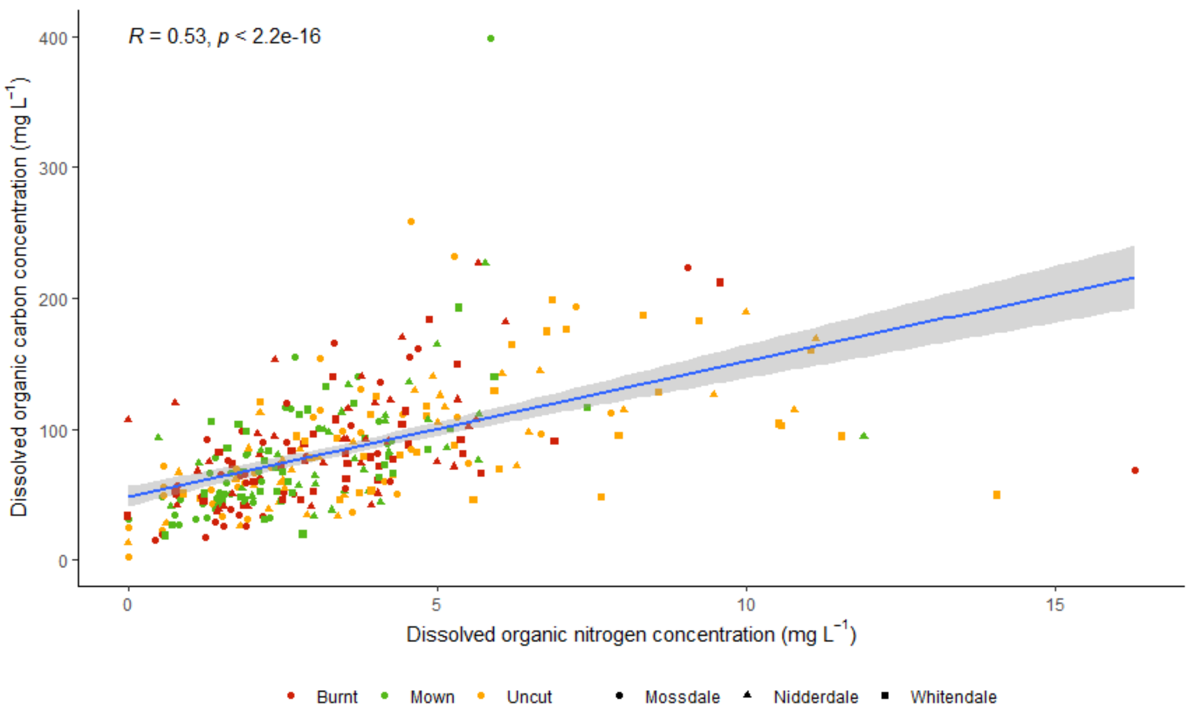


Figure 4.14 Correlation of dissolved organic nitrogen and dissolved organic carbon (mg L^{-1}) in mesocosm porewaters from three grouse moors (Nidderdale, Mossdale, and Whitendale) under three management regimes (burnt, mown and uncut (i.e., nil heather management)). Correlation coefficient displayed.

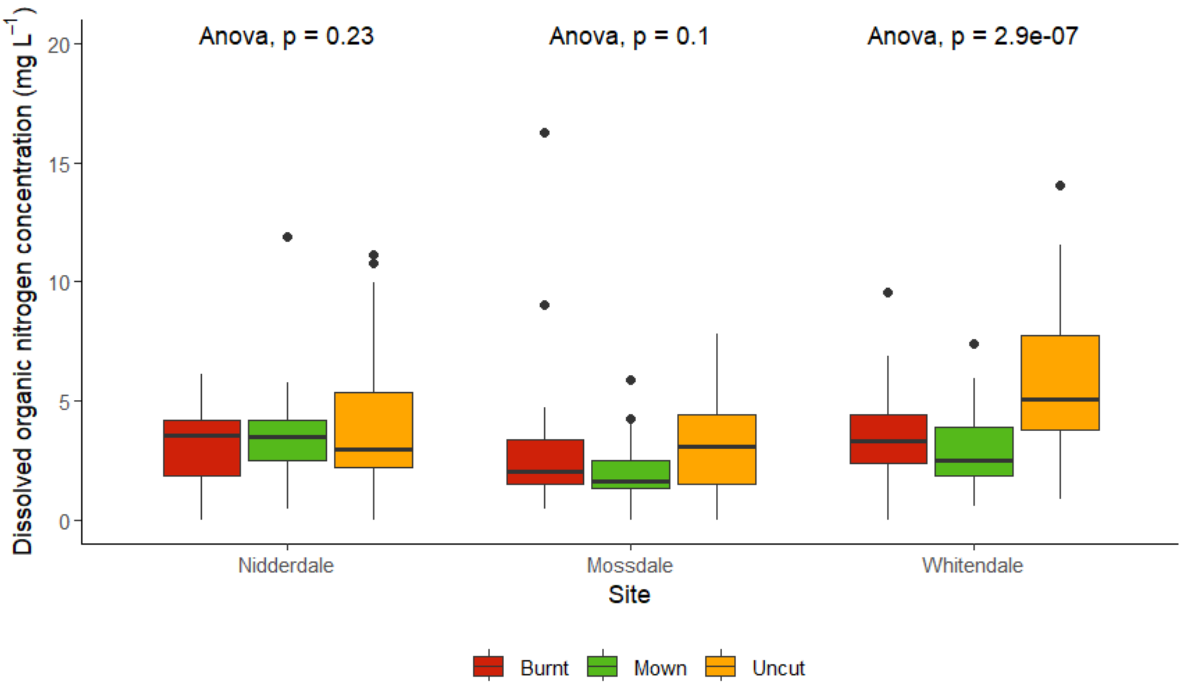


Figure 4.15 Dissolved organic nitrogen concentrations (mg L^{-1}) of mesocosm pore waters from three blanket bog sites (Nidderdale, Mossdale, and Whitendale) under three management regimes (burnt, mown, and uncut). Boxes represent the second and third quartile and the median. Outliers are shown beyond the whiskers. n = 317.

4.3.5.6 UV-vis absorbance

All mesocosm porewaters were scanned for specific wavelengths (UV_{254}, UV_{400}, UV_{465} and UV_{665}) and the majority (reduced due to Covid-19 access restrictions) of central vegetated mesocosm cores were scanned for broad spectrum (230-800 nm) UV absorbance.

4.3.5.6.1 UV_{254} and $SUVA_{254}$

UV_{254} ranged from 0.2 cm^{-1} to 6 cm^{-1} with a median of 3.2 cm^{-1} and a mean of 3.1 ± 1.2 cm^{-1}. There was no significant difference between management regime (ANOVA, F = 1.5, df = 2, $p = 0.22$) but there was a significant difference between site (ANOVA, F = 9.08, df = 2, $p = 0.0001$). Median UV_{254} absorbance was significantly lower in samples from Mossdale compared to Nidderdale and Whitendale (post-hoc $p < 0.05$; median absorbance 2.75 cm^{-1} compared to 3.48 cm^{-1} and 3.6 cm^{-1} respectively). At the site level, there was a significant difference between management regime at Whitendale whereby uncut samples had a significantly higher UV_{254} absorbance compared to mown and burnt cores (median absorbance 3.91 cm^{-1}, 3.37 cm^{-1}, and 3.16 cm^{-1} respectively).

$SUVA_{254}$ ranged from 0.17– 33.60 L^{-1} mg^{-1} m^{-1} with a median of 4.18 ± 1.44 L^{-1} mg^{-1} m^{-1} and a mean of 4.77 ± 2.87 L^{-1} mg^{-1} m^{-1} (Table 4.13). $SUVA_{254}$ did not differ significantly between sites (ANOVA, F=5.25, df = 2, p = 0.53) or management regime (ANOVA, F=0.57, df = 2, p = 0.57; Figure 4.16). There were also no within site differences (Figure 4.16) Cores with *Sphagnum spp*. as their dominant vegetation had the highest median $SUVA_{254}$, but this was not significantly higher to other dominant vegetation cover groups (ANOVA, F = 0.408, df = 4, p = 0.71; Figure 4.17).

Table 4.13 Descriptive statistics for $SUVA_{254}$ (L^{-1} mg^{-1} m^{-1}) of mesocosm central vegetated core pore water from three grouse blanket bogs (Nidderdale, Mossdale, and Whitendale) under three management regimes (burnt, mown, and uncut). SD refers to standard deviation. Number of samples varies per site and treatment due to insufficient water sample collected for analysis.

	Minimum	Maximum	Median	Mean	SD	*n =*
All	0.17	33.60	4.18	4.70	2.87	351
Burnt	0.79	18.96	3.93	4.47	2.83	119
Mown	0.17	17.55	4.36	4.85	2.45	115
Uncut	0.31	33.60	4.20	4.78	3.58	117
Nidderdale	0.65	11.31	4.20	4.46	1.99	117
Mossdale	0.17	33.60	3.94	4.87	3.76	115
Whitendale	0.31	17.55	4.31	4.76	2.56	119

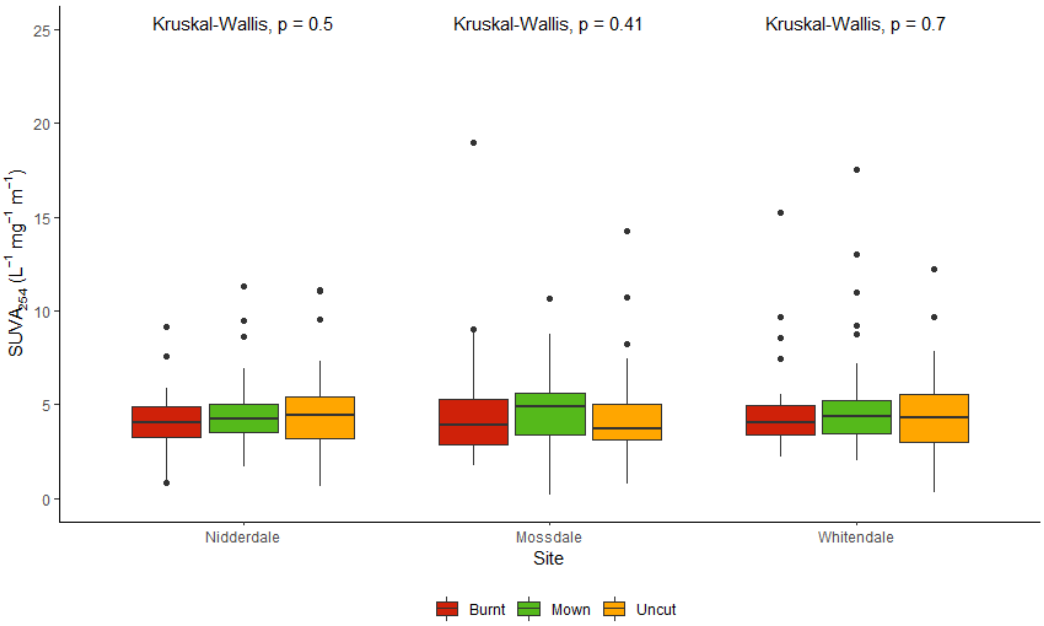


Figure 4.16 $SUVA_{254}$ ($L^{-} mg^{-1} m^{-1}$) of mesocosm pore waters from three blanket bogs (Nidderdale, Mossdale, and Whitendale) under three management regimes (burnt, mown, and uncut). Boxes represent the second and third quartile and the median. Outliers are shown beyond the whiskers. One outlier removed ($SUVA_{254}$ = 33.6) according to statistical analysis methodology.

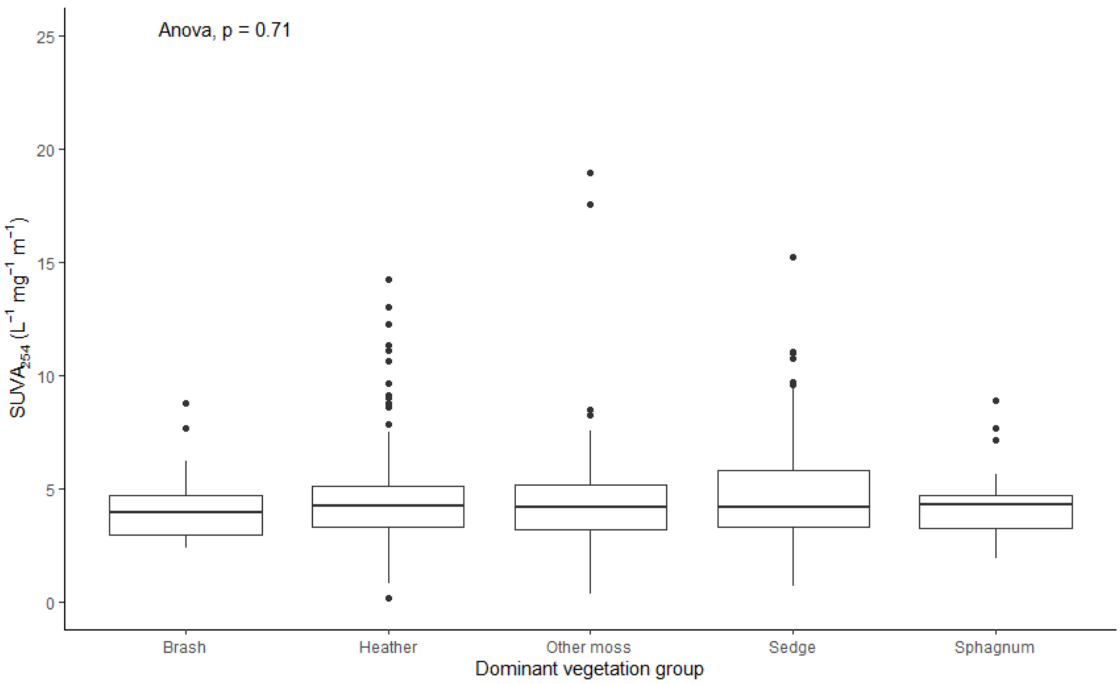


Figure 4.17 Dominant vegetation groups (i.e., vegetation group with the highest % coverage per core) of mesocosm cores from three grouse blanket bog (Nidderdale, Mossdale, and Whitendale) and $SUVA_{254}$ ($L^{-1} mg^{-1} m^{-1}$) of porewaters. Significance test results shown. One outlier removed ($SUVA_{254}$ = 33.6 $L^{-1} mg^{-1} m^{-1}$) according to statistical analysis methodology.

4.3.5.6.2 Other SUVA wavelengths

UV_{280} and UV_{365} abs was obtained during broad-spectrum scanning (all results presented in Chapter 8), however, due to Covid-19 restrictions and sample volumes, not all pore water collections were scanned for broad-spectrum analysis. Therefore, SUVA measurements for wavelengths other than 254 nm and 400 nm have a smaller sample size (168 measurements).

UV_{280} absorbance had a higher correlation for DOC concentration than UV_{254} absorbance (Figure 4.18 A and B; correlation coefficient 0.74 compared to 0.58, $p < 0.01$ respectively) and did not significantly differ between management regime or site (ANOVA, F = 0.996 and 0.294, df = 2, p = 0.372 and 0.745, respectively).

UV_{280} absorbance had a greater correlation for DOC concentration than UV_{254} absorbance (Figure 4.18a and b; correlation coefficient 0.74 compared to 0.58, $p < 0.01$ respectively) and did not significantly differ between management regime or site (ANOVA, F = 0.996 and 0.294, df = 2, p = 0.372 and 0.745, respectively).

$SUVA_{280}$ ranged from 0.34 to 50.85 $m^3\ mg^{-1}\ L$ with a median of 3.37 ± 0.93 $m^3\ mg^{-1}\ L$ and a mean of 3.83 ± 4.02 $m^3\ mg^{-1}\ L$. $SUVA_{280}$ did not significantly differ between management regime or site (ANOVA, F = 0.996 and 0.294, df = 2, p = 0.372 and 0.745,respectively). Median $SUVA_{280}$ was highest in cores dominated by sedge, but this difference was not significant (Figure 4.19). Cores dominated by *Sphagnum* had the lowest median $SUVA_{280}$, but sample size (*n* = 11) was small compared to other vegetation groups (average *n* = 35). Other SUVA wavelengths were investigated (Table 4.14) but no significant differences were found between management regime or site for all wavelengths and there were no discernible trends within the data.

Various wavelength ratios (as reported as useful proxies for DOC composition within the literature; Section 2.8.3 were also investigated). There were no significant differences between management regime or site for each of the ratios (Table 4.14 and Table 4.15).

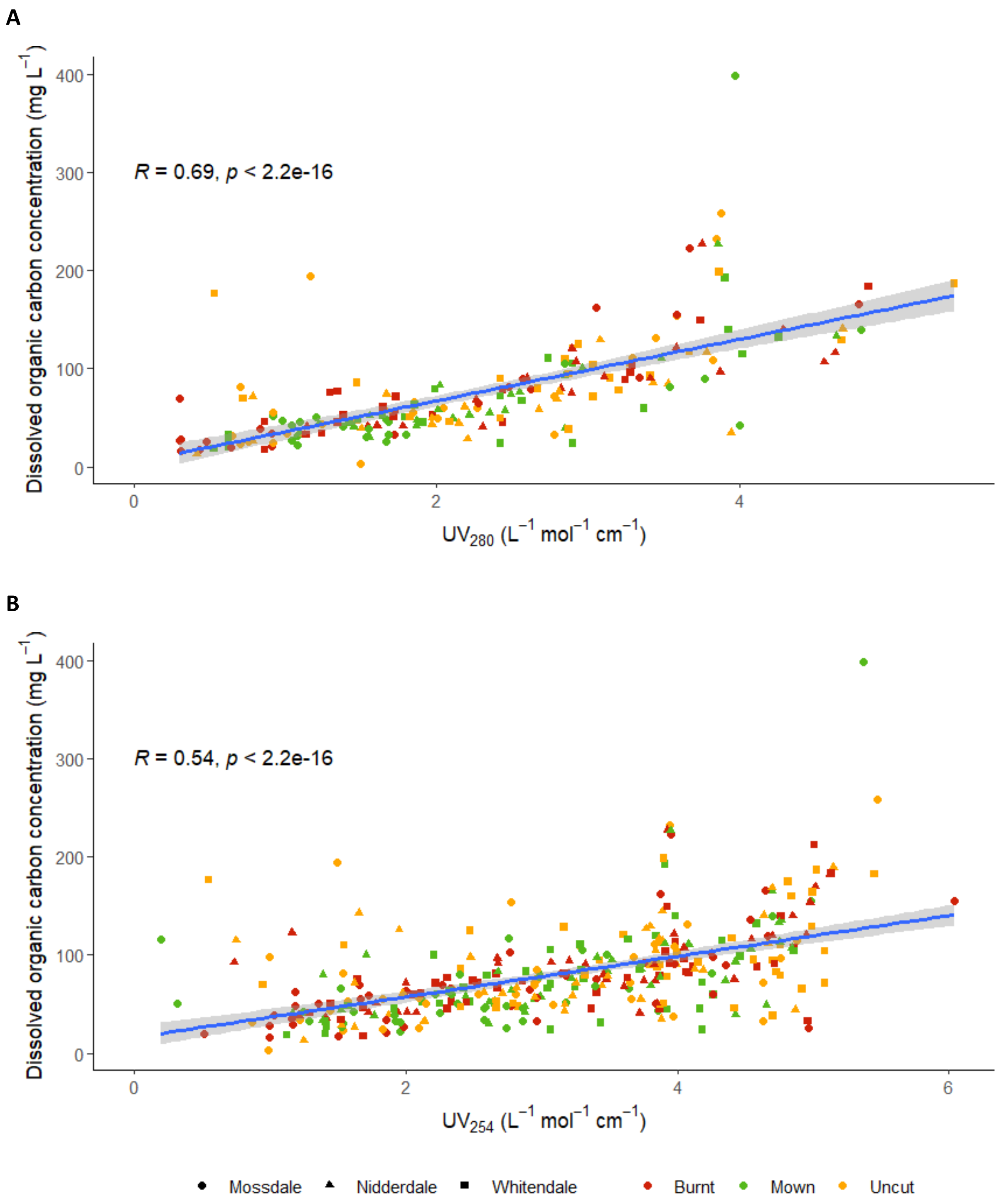


Figure 4.18 Correlation of **A)** 280 nm absorbance and **B)** and 254 nm absorbance vs dissolved organic carbon concentration (mg L^{-1}) of mesocosm pore waters from three grouse blanket bogs (Nidderdale, Mossdale, and Whitendale) under three management regimes (burnt, mown, and uncut (i.e., nil heather management). Correlation coefficient = 0.74 for UV280 and = 0.58 for UV254, $p < 0.01$.

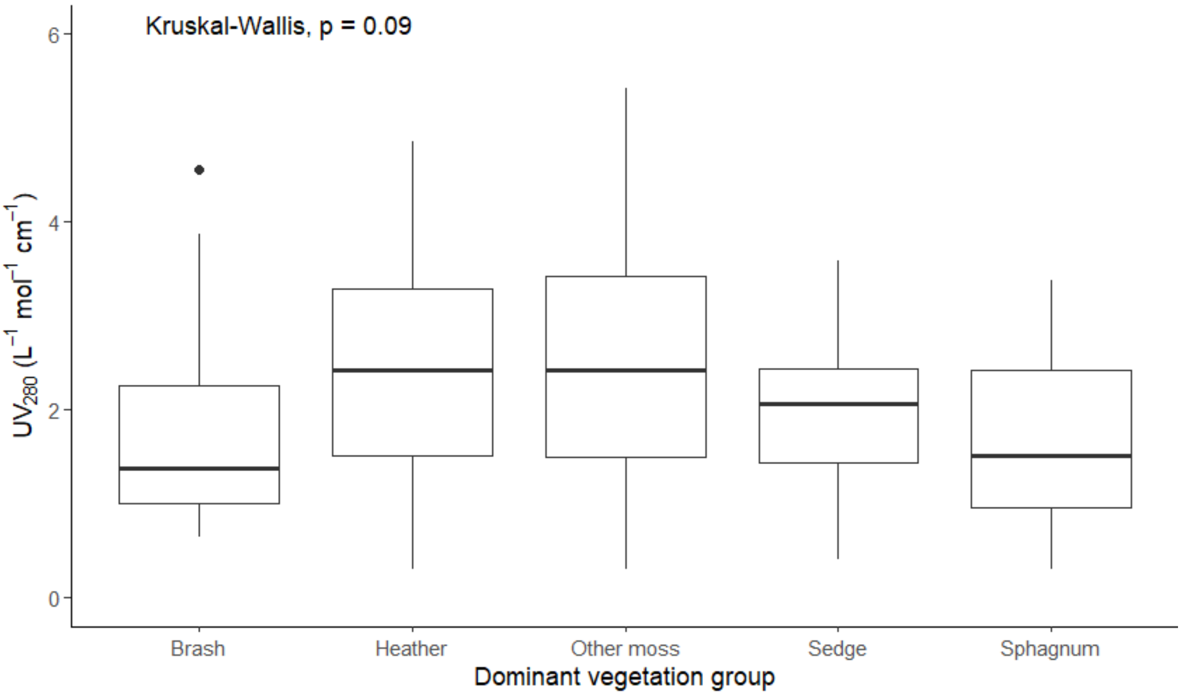


Figure 4.19 Dominant vegetation group and $SUVA_{280}$ of mesocosm porewaters from cores from three grouse blanket bogs (Nidderdale, Mossdale, and Whitendale). Significance test result shown.

Table 4.14 Mean and standard deviation of specific UV absorbance (SUVA) values (m^{-1} mg L^{-1}) of mesocosm pore waters from three grouse-managed UK blanket bog. Burnt, mown and uncut refer to management regimes.

	$SUVA_{254}$	$SUVA_{280}$	$SUVA_{365}$	$SUVA_{400}$
All	4.70 ± 2.86	3.66 ± 3.74	1.28 ± 1.24	0.71 ± 0.48
Burnt	4.47 ± 2.38	3.08 ± 1.10	1.09 ± 0.49	0.68 ± 0.50
Mown	4.85 ± 2.45	4.01 ± 1.93	1.30 ± 0.78	0.70 ± 0.36
Uncut	4.78 ± 3.58	3.40 ± 1.45	1.47 ± 1.93	0.75 ± 0.55
Nidderdale	4.46 ± 1.99	2.52 ± 1.01	0.88 ± 0.42	0.69 ± 0.36
Mossdale	4.86 ± 3.76	2.77 ± 1.19	1.23 ± 0.62	0.70 ± 0.60
Whitendale	4.76 ± 2.56	3.23 ± 1.93	1.79 ± 0.87	0.75 ± 0.48

Table 4.15 Mean and standard deviation of spectroscopic ratios of mesocosm pore waters from three grouse blanket bog (Nidderdale, Mossdale, and Whitendale). Burnt, mown and uncut refer to management regimes.

	E_{250}/E_{365}	E_{254}/E_{436}	E_{365}/E_{465}	E_{465}/E_{665}
All	3.79 ± 2.50	16.16 ± 11.16	5.27 ± 2.92	6.03 ± 7.21
Burnt	4.16 ± 3.77	18.61 ± 15.40	5.10 ± 2.53	6.23 ± 7.98
Mown	3.69 ± 2.69	15.94 ± 9.26	5.71 ± 3.13	4.75 ± 2.69
Uncut	3.56 ± 1.68	14.12 ± 6.88	5.10 ± 2.95	7.06 ± 8.96
Nidderdale	4.09 ± 3.71	18.91 ± 14.90	5.37 ± 3.08	6.72 ± 9.11
Mossdale	3.83 ± 1.95	14.33 ± 9.44	5.21 ± 3.48	6.23 ± 3.21
Whitendale	3.46 ± 0.96	15.13 ± 6.97	5.23 ± 2.07	5.13 ± 7.82

4.3.5.6.3 Hazen

Hazen ranged from 13 – 1427 with a median of 368 ± 227 and a mean of 428 ± 267. Hazen differed significantly between sites (ANOVA, F = 7.72, df = 2, p = 0.0005) but not between management regimes (ANOVA, F = 2.65, df = 2, p = 0.07). Hazen of Mossdale porewaters was significantly lower than Nidderdale and Whitendale (post-hoc Tukey p = 0.02 and p < 0.0004 respectively). Uncut samples had a higher hazen than mown and burnt samples (470 ± 293 compared to 394 ± 232 and 418 ± 264 respectively; Table 4.16) however, this difference was not significant (ANOVA, F = 2.504, df = 2, p = 0.08). There were no within site differences at Nidderdale and Mossdale, but at Whitendale, uncut samples had significantly higher hazen values than mown samples (ANOVA, F= 2.839, df = 4, p = 0.02, post-hoc Tukey p = 0.004).

Table 4.16 Descriptive statistics for Hazen of mesocosm central vegetated core pore water from grouse managed blanket bog sites (Nidderdale, Mossdale, and Whitendale; burnt, mown, and uncut). SD refers to standard deviation. Number of samples varies per site and treatment due to insufficient sample volume collected for analysis.

	Minimum	Maximum	Median	Mean	SD	*n =*
All	13.3	1426.7	319.6	426.7	267.4	351
Burnt	57.5	1286.3	320.4	418.1	265.5	119
Mown	13.3	1295.8	298.4	390.9	234.8	115
Uncut	79.2	1426.7	347.9	470.6	294.3	117
Nidderdale	95.8	1373.6	347.6	445.2	248.1	117
Mossdale	13.3	1295.8	274.9	349.8	248.1	115
Whitendale	86.6	1426.7	360.6	482.8	289.4	119

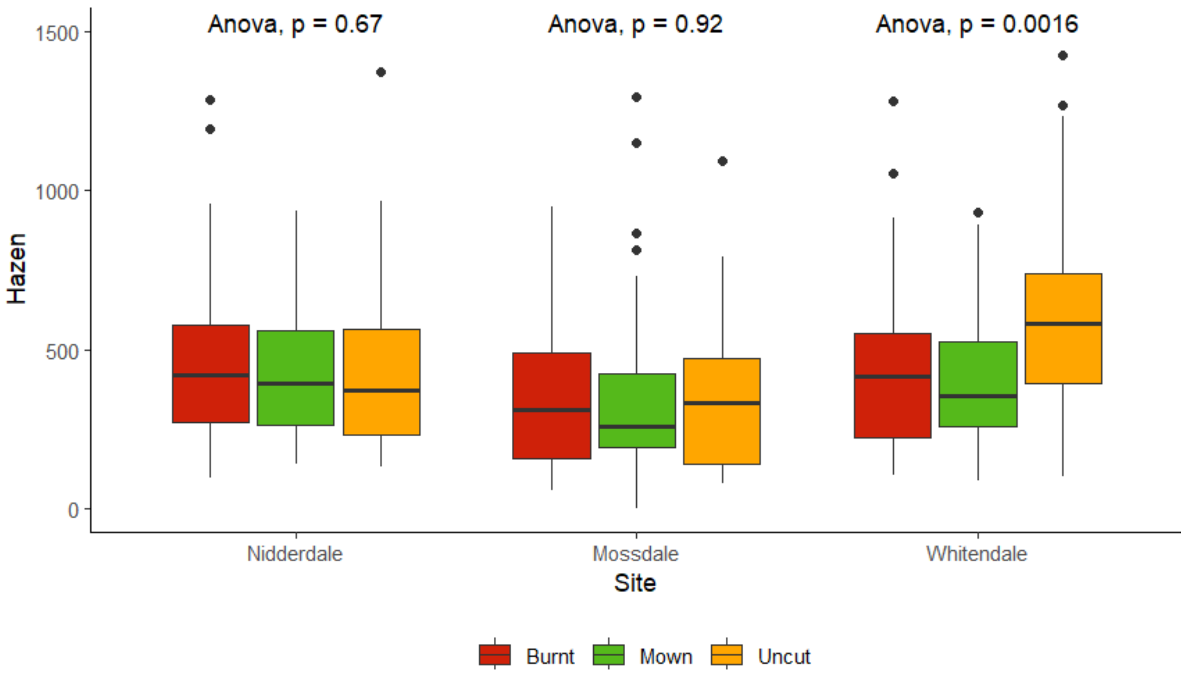


Figure 4.20 Hazen of mesocosm pore waters from three blanket bog sites (Nidderdale, Mossdale, and Whitendale) under three management regimes (burnt, mown and uncut). Boxes represent the second and third quartile and the median. Outliers are shown beyond the whiskers.

4.3.5.7 pH

The pH of porewater samples ranged from 3.24 – 5.55 with a median of 4.02 ± 0.29 and mean of 4.04 ± 0.31. pH did not differ significantly between management regime (ANOVA, F = 0.129, df = 2, p = 0.88) or site (ANOVA, F= 0.25, df = 2, p = 0.78). There were no significant differences between management regime at the site level (Figure 4.21).

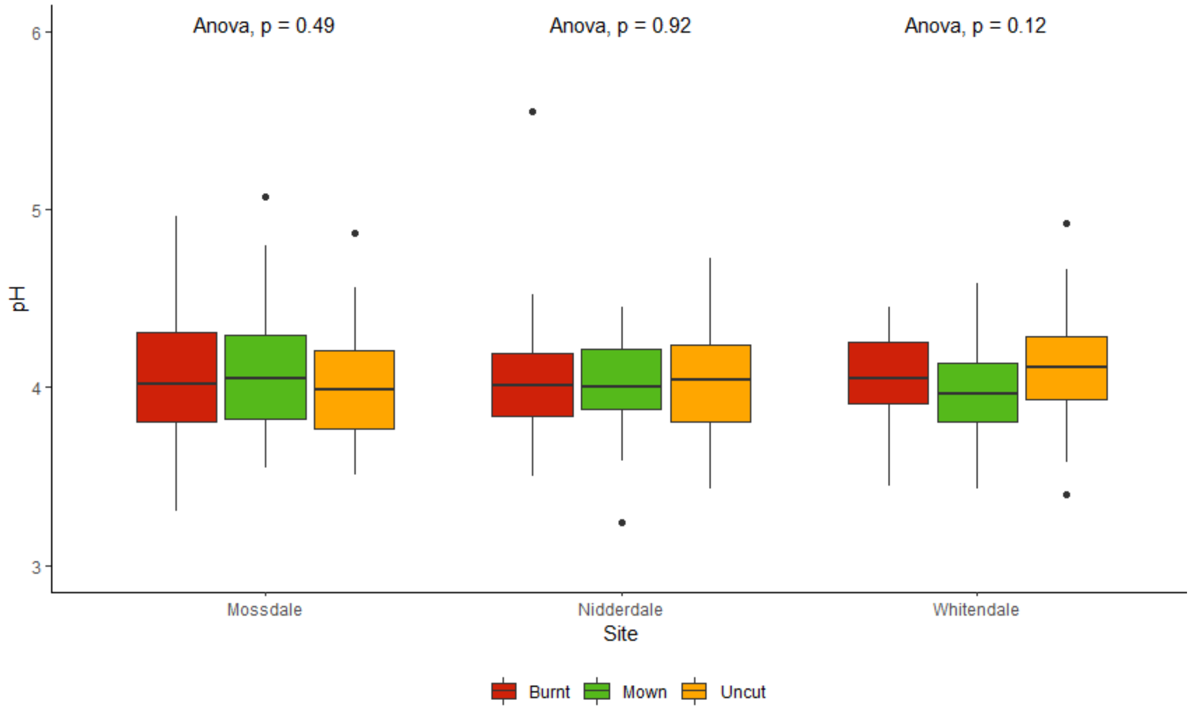


Figure 4.21 pH of mesocosm pore waters from three blanket bog sites (Nidderdale, Mossdale, and Whitendale). Boxes represent the second and third quartile and the median. Outliers are shown beyond the whiskers. Significance testing results shown. Burnt, mown and uncut refer to the three management regimes.

Porewater pH differed significantly with season (ANOVA, F = 8.73, df = 8, $p < 0.01$) with warmer months generally showing a lower pH (Figure 4.22) and an overall negative correlation with soil temperature (Spearman's correlation, R = -0.48, $p < 0.01$; Figure 4.22). Although pH is known to be a significant control on porewater chemistry, pH was only significantly correlated with DOC concentration (albeit with a low R-value) and correlations between the absorbance of wavelengths commonly employed by the water industry (i.e., $SUVA_{254}$, Hazen and E4:E6) were not significant (Table 4.17).

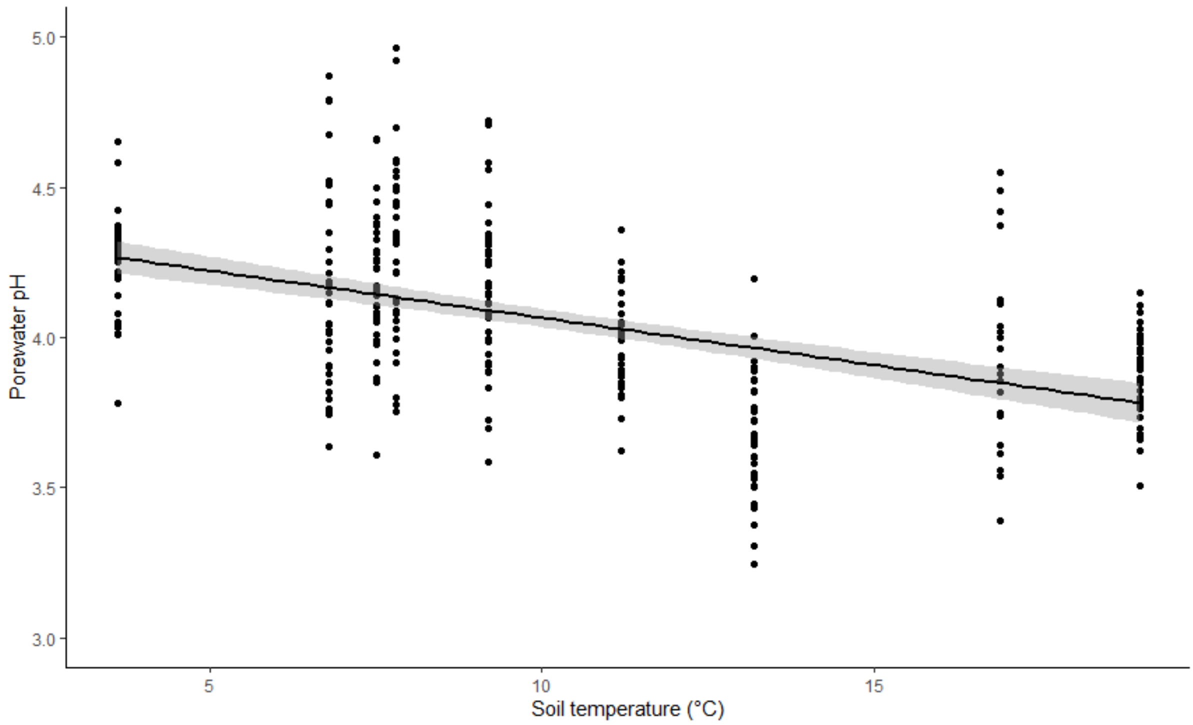


Figure 4.22 Correlation of soil temperature (°C) and porewater pH of mesocosm porewater samples. Line of best fit shown. A single soil temperature measurement was used for each porewater collection. Spearman's correlation = R = -0.48, p < 0.01.

Table 4.17 Correlations between mesocosm porewater pH and water quality parameters commonly used by the water industry in drinking water treatment. Significant correlations are shown in bold.

Water quality parameter	Correlation
DOC concentration	**R = -0.15, p < 0.05**
$SUVA_{254}$	R = 0.02, p = 0.79
Hazen	R = 0.078, p = 0.15
E4:E6	R = 0.06, p = 0.29

The pH of mesocosm porewaters was comparable to those measured in the field (as reported in Heinemeyer *et al.*, 2023; Table 4.18), but there is a smaller difference between the mean pH of the management regimes in the mesocosm cores compared to the field.

Table 4.18 pH of mesocosm pore waters of cores from three grouse blanket bog under three management regimes (burnt, mown and uncut). Field site pH measurements reported in Heinemeyer *et al.*, 2023).

Management	pH
Mesocosm	
Burnt	4.05 ± 0.33
Mown	4.04 ± 0.31
Uncut	4.06 ± 0.32
Field site	
Burnt	4.26 ± 0.068
Mown	4.10 ± 0.077
Uncut	4.16 ± 0.068

4.3.5.8 Conductivity

Conductivity was measured in 336 samples and ranged from 17.61 – 381.00 µS cm^{-1} with a median of 99.07 ± 56.52 µS cm^{-1} and a mean of 114.23 ± 65.89 µS cm^{-1}. There were no significant differences between management regimes (KW chi squared = 5.51, df = 2, p = 0.06) nor sites (KW chi-squared = 0.24, df = 2, p = 0.88) and no significant differences were observed within sites (Figure 4.23).

Conductivity varied significantly between seasons (ANOVA, F = 58.12, df = 3, $p < 0.01$) with porewaters collected in summer having higher median conductivity compared to other seasons. Significant differences were shown between all seasons (Post-hoc Tukey, $p < 0.05$) apart from Spring-Winter. However, when comparing management regime seasonally, there were no differences between burnt, mown and uncut cores (Figure 4.24).

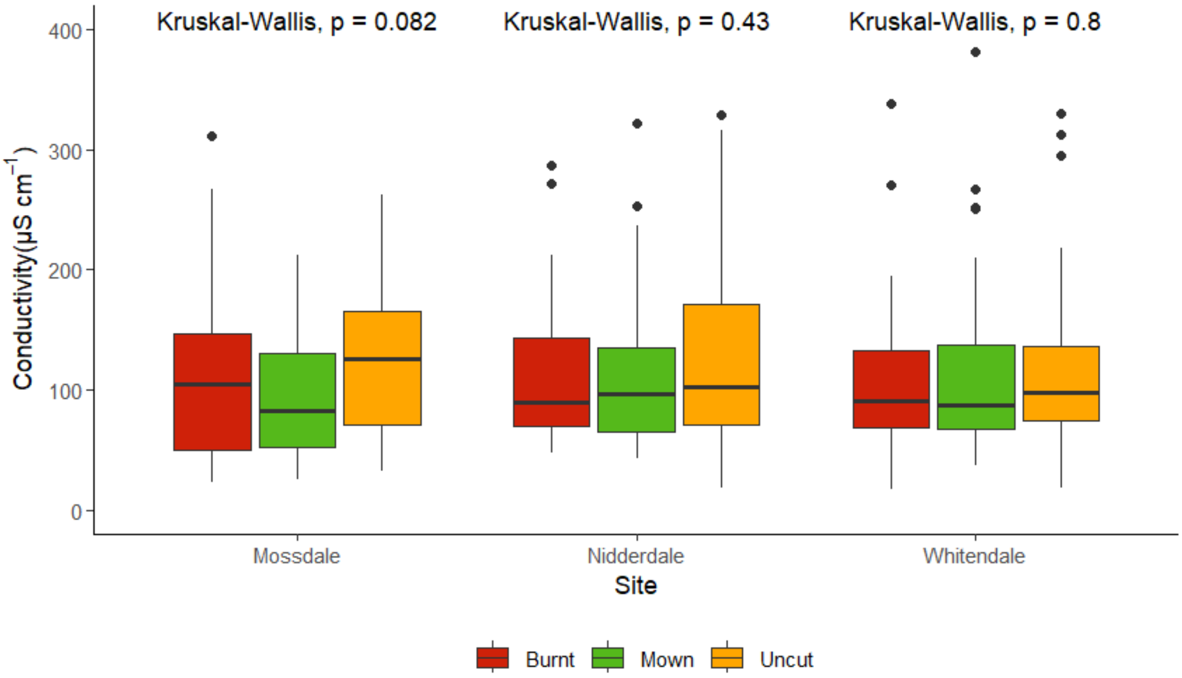


Figure 4.23 Conductivity (µS cm^{-1}) of mesocosm pore waters of peat soil cores taken from three grouse-managed blanket bogs (Nidderdale, Mossdale, and Whitendale) from burnt, mown and uncut management regime mesocosms. Significant testing shown.

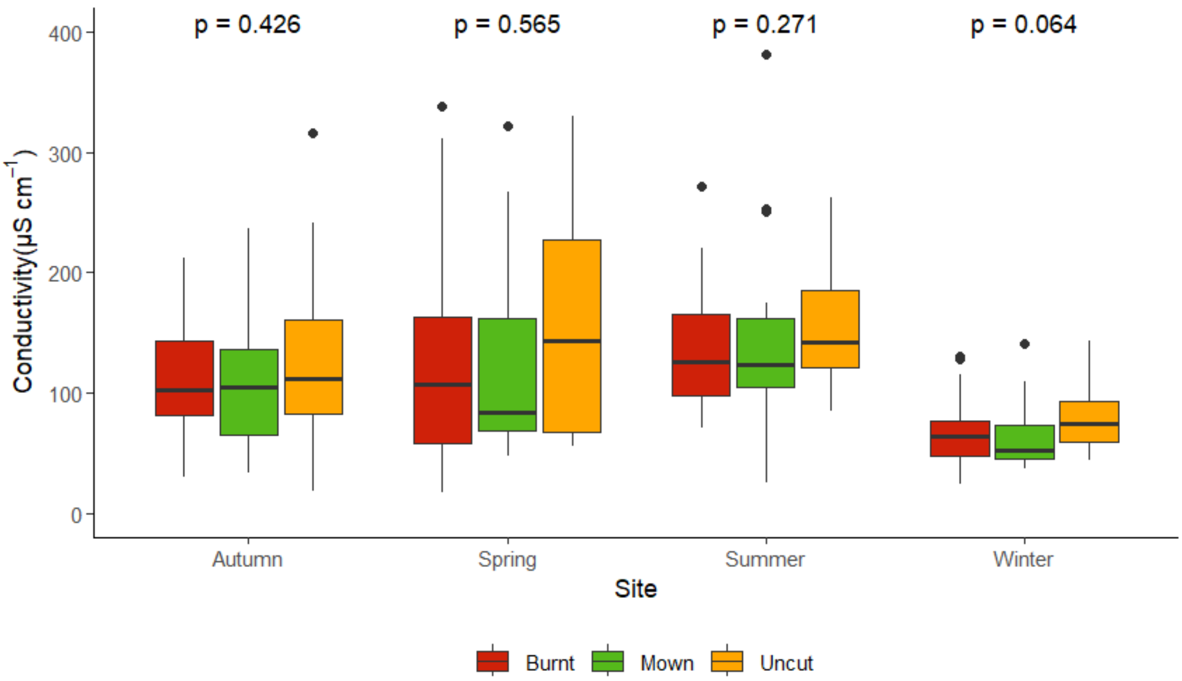


Figure 4.24 Seasonal conductivity of mesocosm pore waters. Winter included collections in November, December, and January, Spring collections in February, March, April and henceforth. Outliers shown beyond the whiskers. Significance test (KW chi-squared) results shown.

4.3.6 Gas Fluxes

4.3.6.1 Soil Respiration (SR)

SR of uncut side cores (i.e., root + microbial respiration) ranged from 0.01 – 8.8 µmol CO_2 m^{-2} s^{-1} with a median of 1.18 µmol CO_2 m^{-2} s^{-1} whilst cut side cores (microbial respiration) ranged from 0.01 – 10.66 µmol CO_2 m^{-2} s^{-1} with a median of 0.81 µmol CO_2 m^{-2} s^{-1}. There was no significant difference in SR of uncut side cores between management regime (KW chi-squared, df = 2, $p = 0.72$) nor site (Kruskal Wallis chi-squared = 2.24, df = 2, $p = 0.33$; Figure 4.25 A). Similarly, there were no significant differences between management (KW chi-squared = 0.41, df = 2, $p = 0.81$) nor site (KW chi-squared = 3.4, df = 2, $p = 0.18$) in cut core SR (Figure 4.25 B). Mesocosm SR was higher than measurements reported for the field site (Heinemeyer *et al*., 2023); however, for roots + decomposition SR flux, uncut plots had the highest mean flux and mown the lowest in both the mesocosms and in the field (Table 4.19).

WTD was significantly correlated with SR ($p < 0.01$, method = Spearman) albeit with R = 0.13.m Root respiration (i.e., difference between uncut and cut side cores) ranged from 0.01 µmol CO_2 m^{-2} s^{-1} – 7.82 µmol CO2 m^{-2} s^{-1} with a median of 0.88 µmol CO_2 m^{-2} s^{-1} and did not differ significantly between management regime (KW chi-squared = 1.56, df = 2, $p = 0.46$) or site (KW chi-squared = 4.41, df = 2, $p = 0.11$). Root respiration was significantly correlated with % *C. vulgaris* coverage ($p = 0.02$), albeit with a low correlation coefficient ($R = 0.11$). SR was significantly positively correlated with soil temperature ($R = 0.80$, $p < 0.01$) as shown in Figure 4.26. Root respiration was similarly positively correlated albeit less strongly ($R = 0.28$, $p < 0.01$).

Table 4.19 Mean soil respiration C fluxes (µmol CO_2 m^{-2} s^{-1}; for roots + decomposition and decomposition only) for mesocosm cores and plots in the field site at three grouse blanket bog (Nidderdale, Mossdale, and Whitendale) under three management regimes (burnt, mown, and uncut). Standard deviation shown.

Management	Roots + decomposition flux (µmol CO_2 m^{-2} s^{-1})	Decomposition flux (µmol CO_2 m^{-2} s^{-1})
Mesocosm		
Burnt	1.54 ± 1.31	1.10 ± 1.27
Mown	1.47 ± 1.43	1.06 ± 1.04
Uncut	1.56 ± 1.44	1.06 ± .094
In-field measurements		
Burnt	0.89 ± 0.85	0.86 ± 0.80
Mown	0.86 ± 0.80	0.77 ± 0.65
Uncut	0.97 ± 0.81	0.79 ± 0.65

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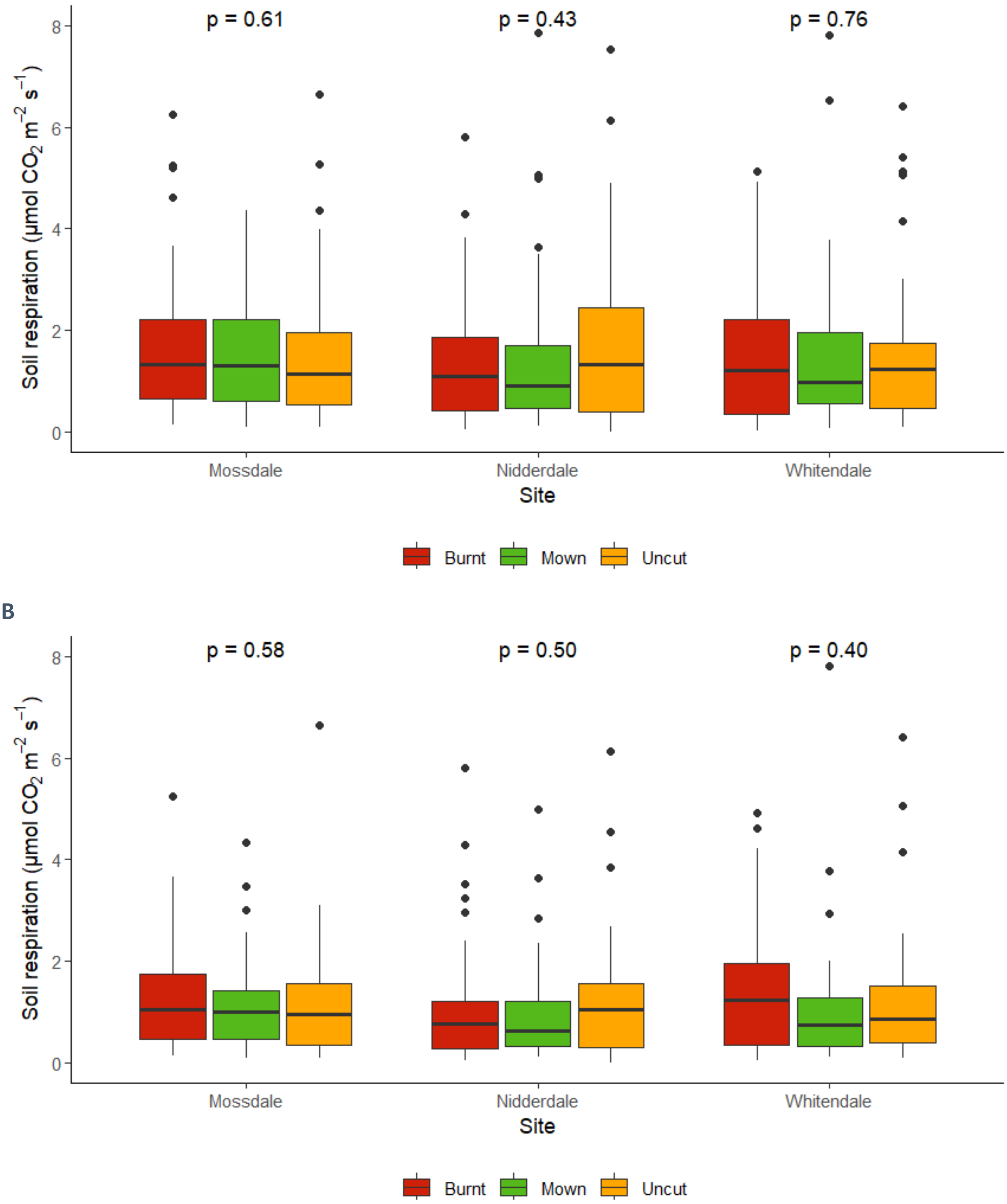


Figure 4.25 Soil respiration (µmol CO_2 m^{-2} s^{-1}) of **A)** uncut (i.e., root and microbial respiration) and **B)** cut (i.e., microbial respiration) side mesocosm cores from three grouse-moor blanket bog (Nidderdale, Mossdale and Whitendale) under different management regimes. Kruskal Wallis test indicated no within site differences. Outliers shown beyond the whiskers.

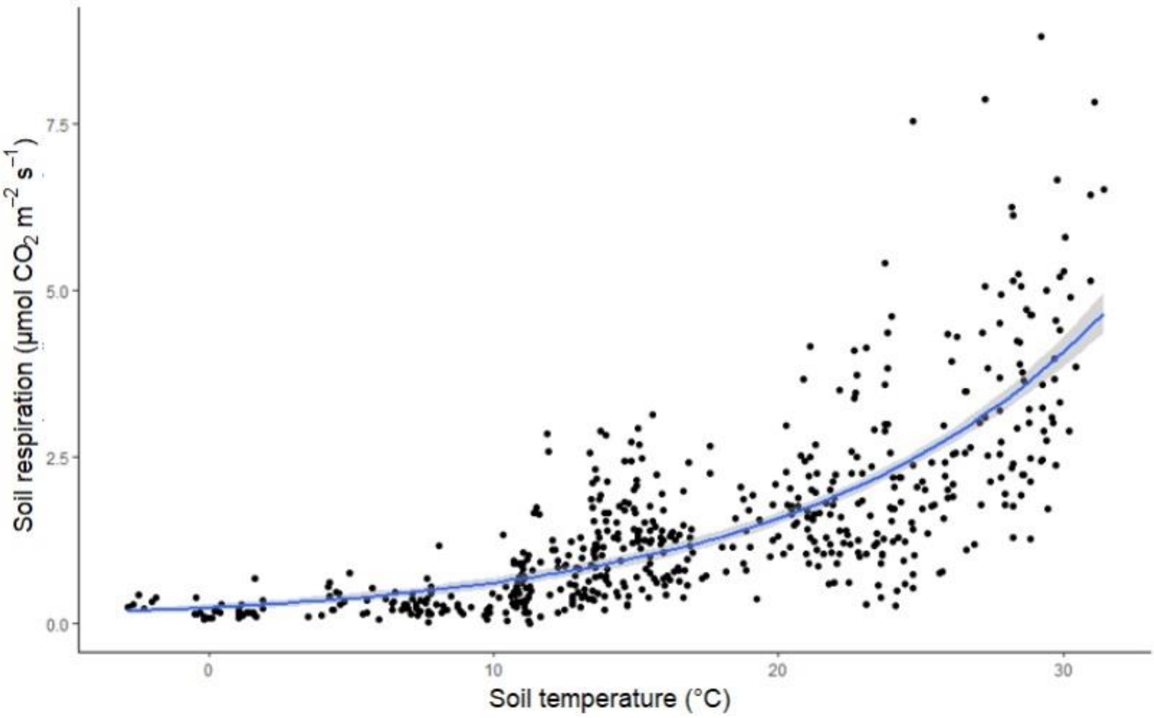


Figure 4.26 Correlation of soil temperature (°C) and soil respiration (µmol CO_2 m^{-2} s^{-1}) of uncut mesocosm side cores from three grouse-blanket bog. Line of best fit plotted with 95% confidence interval (shaded area).

4.3.6.2 Full light net ecosystem exchange (NEE)

NEE ranged from -19.87 – 3.28 µmol CO_2 m^{-2} s^{-1} with a median of -3.24 µmol CO_2 m^{-2} s^{-1} and a mean of -4.52 ± 4.10 µmol CO_2 m^{-2} s^{-1} (negative values represent CO_2 uptake; Table 5.20). During full light measurements, the PAR ranged from 38.39 – 1892.46 and chamber air temperatures were similar between pairs of full light and R_{eco} measurements (difference of less than 5°C). Burnt cores had the lowest median NEE, whilst uncut cores had the highest (-2.93 µmol CO_2 m^{-2} s^{-1} and -3.79 µmol $CO_2$$m^{-2}$ s^{-1} respectively); however, there were no significant differences between management regimes (KW chi-squared, F = 4.93, df = 2, p = 0.08). Median NEE was significantly lower in Mossdale (-4.40 µmol CO_2 m^{-2} s^{-1}) cores than in Nidderdale (-2.95 µmol CO_2 m^{-2} s^{-1} µmol CO_2 m^{-2} s^{-1}) and Whitendale (-3.02 µmol CO_2 m^{-2} s^{-1}) cores (Kruskal Wallis chi-squared =18.77, df = 2, p < 0.01; pairwise Wilcoxon test p < 0.01). Uncut cores from Mossdale had a significantly lower NEE compared to mown and burnt cores; however, this within site difference was not present in cores from the other sites (Figure 4.27). CH_4 and NEE flux were not significantly correlated (R = -0.02, p = 073).

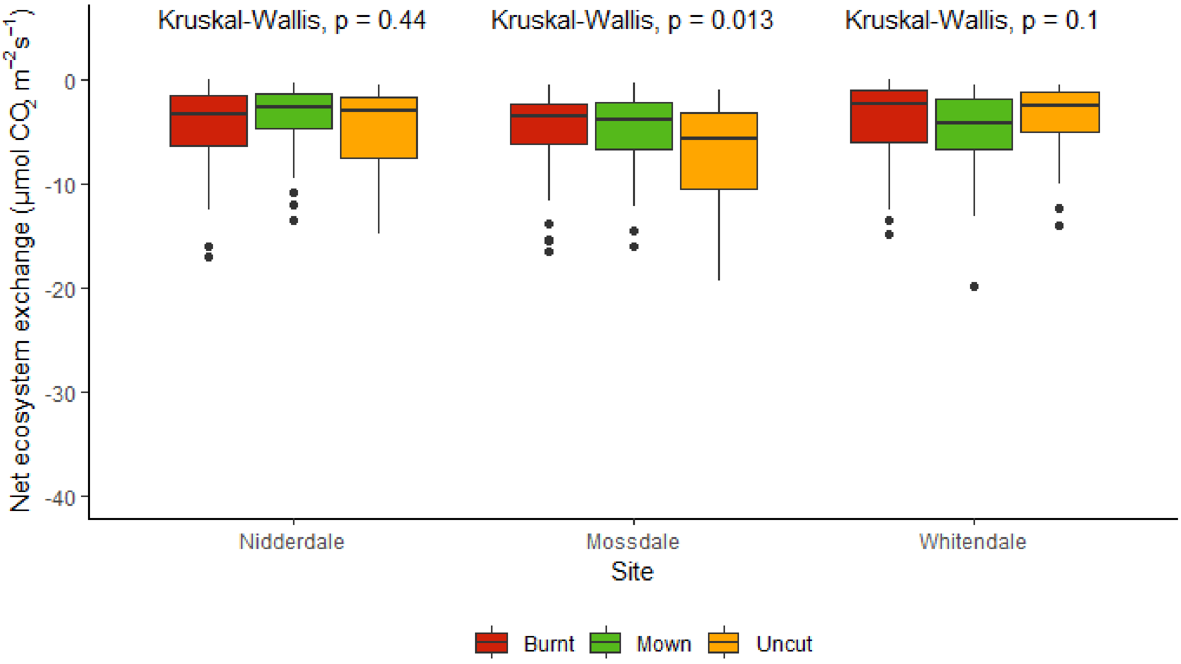


Figure 4.27 Full light net ecosystem exchange for mesocosm cores taken from grouse-managed blanket bog (Nidderdale, Mossdale, and Whitendale) under three management regimes (burnt, mown, and uncut). One anomalous result removed (NEE < -20 µmol CO_2 m^{-2} s^{-1}).

Table 4.20 Descriptive statistics for full light net ecosystem exchange (µmol CO_2 m^{-2} s^{-1}) of mesocosm cores from grouse managed blanket bog sites (Nidderdale, Mossdale, and Whitendale) under three management regimes (burnt, mown, and uncut). SD refers to standard deviation.

	Minimum	Maximum	Median	Mean	SD	*n =*
All	-19.87	3.28	-3.24	-4.51	4.10	456
Burnt	-16.97	3.28	-2.93	-4.12	4.02	151
Mown	-19.87	1.32	-3.22	-4.32	3.83	152
Uncut	-19.33	0.49	-3.76	-5.11	4.40	153
Nidderdale	-16.97	1.86	-2.87	-4.14	3.72	151
Mossdale	-19.33	1.6	-4.11	-5.56	4.63	151
Whitendale	-19.87	3.28	-2.92	-3.84	3.71	154

4.3.6.3 Ecosystem respiration (*R_{eco}*)

R_{eco} ranged from 0.22 – 34.89 µmol CO_2 m^{-2} s^{-1} with a median of 3.16 µmol CO_2 m^{-2} s^{-1} and a mean of 4.15 ± 3.67 µmol CO_2 m^{-2} s^{-1}. Median R_{eco} was lowest in mown cores, but this difference was not significant (KW chi-squared = 2.81, df = 2, p = 0.24) compared to burnt and uncut cores. Burnt cores had the highest median R_{eco} (Table 4.21). R_{eco} of Mossdale cores was significantly higher (median 4.06 µmol CO_2 m^{-2} s^{-1}) compared to Nidderdale and Whitendale cores (KW chi-squared = 19.93, df = 2, p < 0.01, post-hoc p < 0.01; median 1.81 µmol CO_2 m^{-2} s^{-1} and 2.95 µmol CO_2 m^{-2} s^{-1}). There were no significant within site differences (Figure 4.28). Larger R_{eco} fluxes were associated most significantly with cores dominated by *C. vulgaris* and brash (Figure 4.29; ANOVA, F = 6.26, df = 4, p < 0.001; Figure 4.29).

Table 4.21 Descriptive statistics for ecosystem respiration (R_{eco}; µmol CO_2 m^{-2} s^{-1}) of mesocosm cores from three grouse managed (burnt, mown, and uncut) blanket bog sites (Nidderdale, Mossdale, and Whitendale). SD refers to standard deviation.

	Minimum	Maximum	Median	Mean	SD	*n =*
All	-13.48	34.89	2.82	3.61	4.66	469
Burnt	0.24	20.19	3.36	4.47	3.71	156
Mown	0.22	34.89	3.34	4.21	3.88	156
Uncut	0.31	22.18	2.71	3.77	3.36	157
Nidderdale	0.33	16.66	2.53	3.54	2.81	157
Mossdale	0.22	22.18	4.06	5.15	4.18	156
Whitendale	0.22	34.89	2.95	3.86	3.79	156

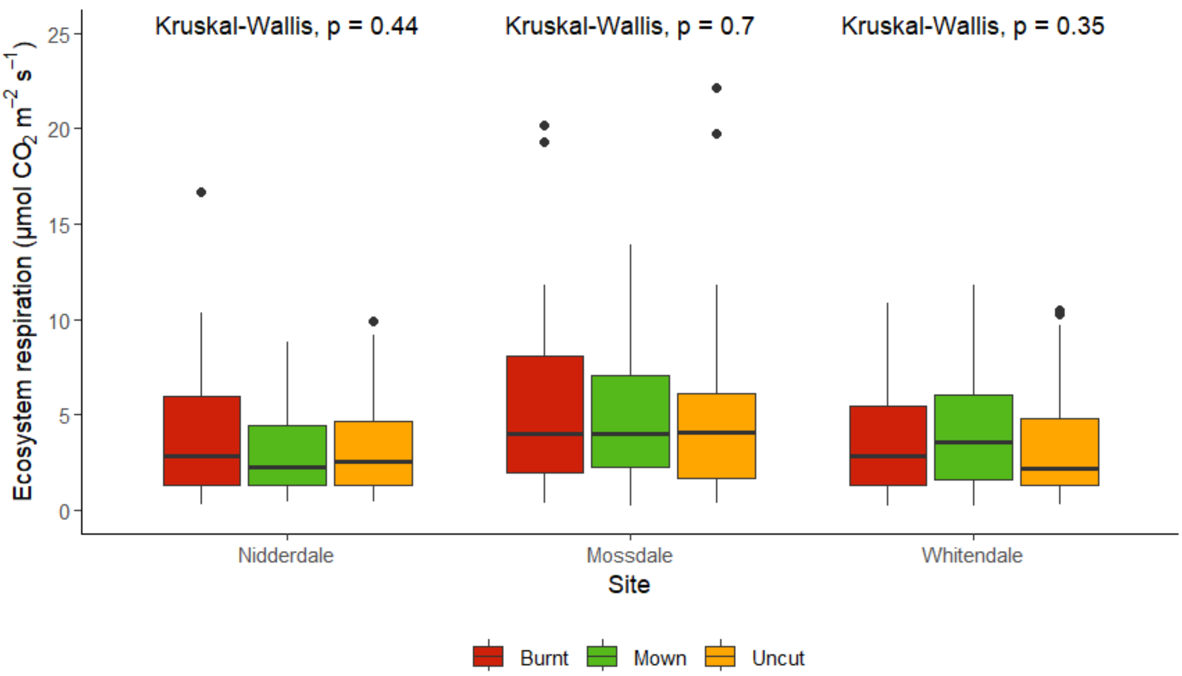


Figure 4.28 Ecosystem respiration for mesocosm cores taken from grouse-managed blanket bog (Nidderdale, Mossdale, and Whitendale) under three management regimes (burnt, mown, and uncut). Significance testing result shown.

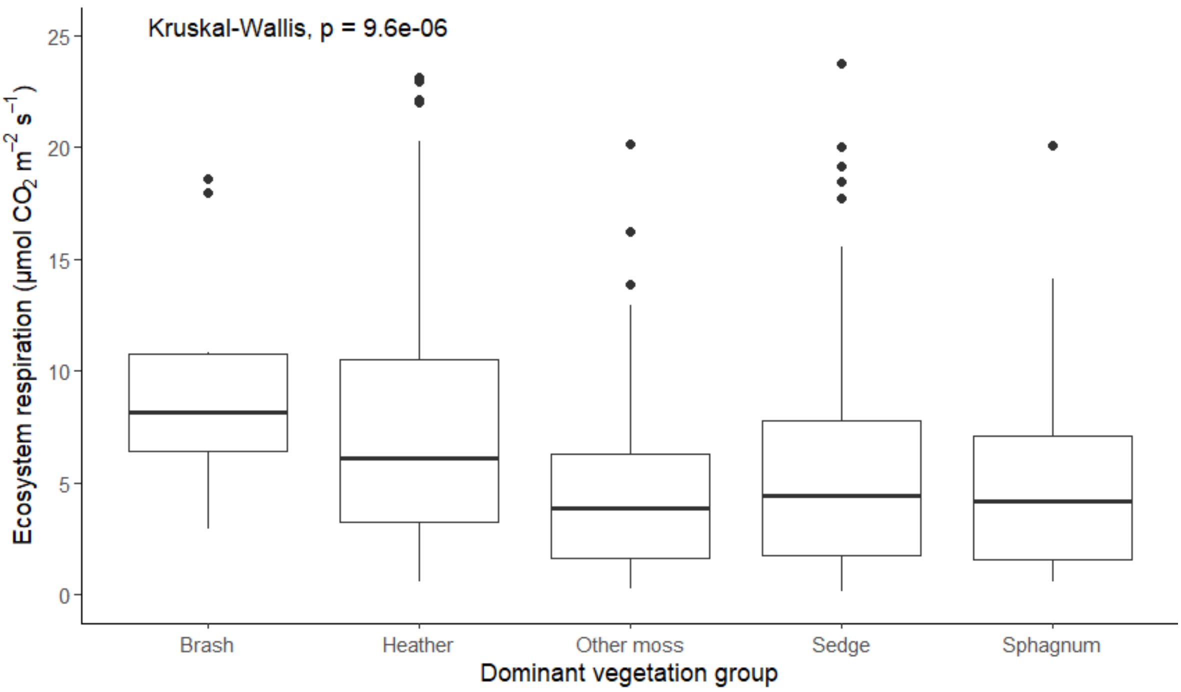


Figure 4.29 Ecosystem respiration (R_{eco}) for mesocosm cores dominated by different vegetation groups from grouse-managed blanket bog (Nidderdale, Mossdale, and Whitendale) under three management regimes (burnt, mown, and uncut). Significance testing result shown.

R_{eco} was comparable between field (2019-2022 measurements) and mesocosm measurements (KW chi-squared = 0.31, df = 1, p = 0.5) with median field and mesocosm R_{eco} being 2.91 µmol CO_2 m^{-2} s^{-1} and 3.17 µmol CO_2 m^{-2} s^{-1} respectively. However, field measurements from uncut plots were significantly higher compared to their mesocosm counterparts (Mann Whitney W = 18290, p < 0.001; Figure 4.30).

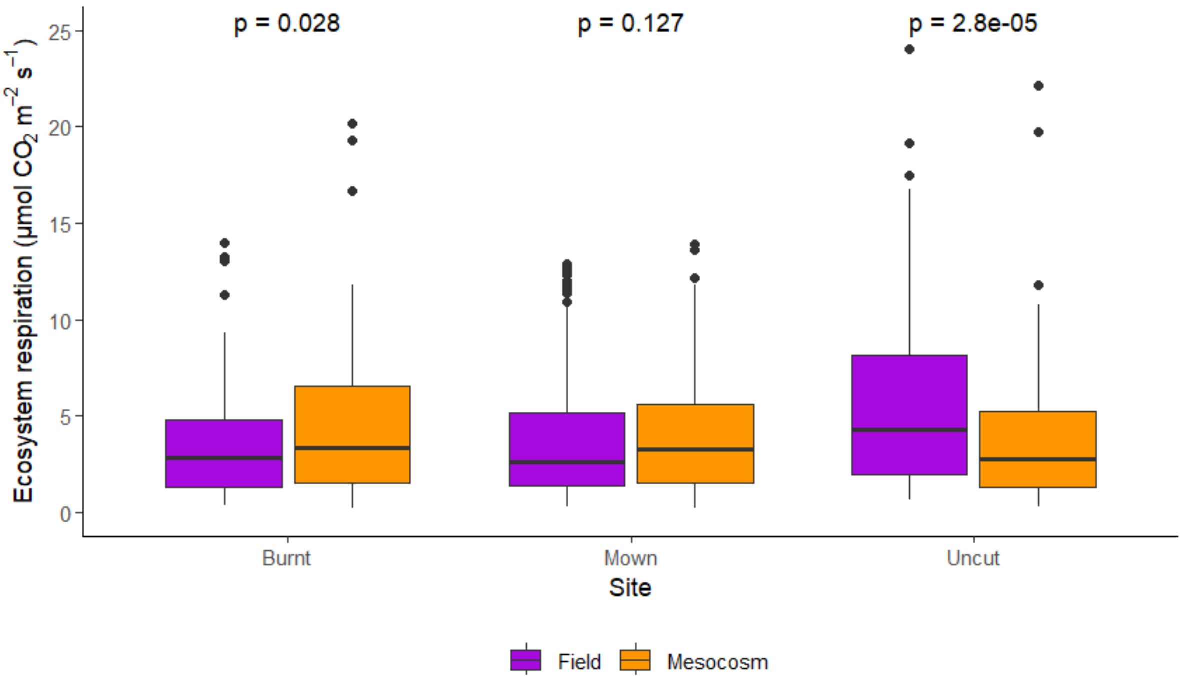


Figure 4.30 Ecosystem respiration (R_{eco}; µmol CO_2 m^{-2} s^{-1}) comparison between field and mesocosm measurements from three grouse moors (Nidderdale, Mossdale, and Whitendale) under three management regimes (burning, mowing and uncut). Statistical test result shown.

4.3.6.4 Methane (CH_4)

In full light conditions, CH_4 flux ranged from 0.001 to 1256 nmol CH_4 m^{-2} s^{-1} with a median of 13.82 nmol CH_4 m^{-2} s^{-1}. There were significant differences in CH_4 flux between management regime (KW chi-squared – 45.83, df = 2, p < 0.01, post-hoc testing p < 0.01) and between sites (KW chi-squared = 24.59, df = 2, p < 0.01, post-hoc testing p < 0.01). The median CH_4 flux was greatest in mown cores (27.33 nmol CH_4 m^{-2} s^{-1}) and lowest in uncut cores (5.97 nmol CH_4 m^{-2} s^{-1}). It was greatest in cores from Mossdale (23.39 nmol CH_4 m^{-2} s^{-1}) and lowest in cores from Whitendale (6.30 nmol CH_4 m^{-2} s^{-1}). CH_4 flux was significantly higher in mown cores in all seasons excluding winter (Figure 4.32). Within site differences were found at each site, and uncut had the lowest median flux at each site. GLM modelling indicated that no vegetation type was significantly associated with a higher CH_4 flux (p >

0.05, AIC = 6748.35); however, CH_4 flux was significantly correlated with % sedge coverage (R = 0.22, p < 0.01).

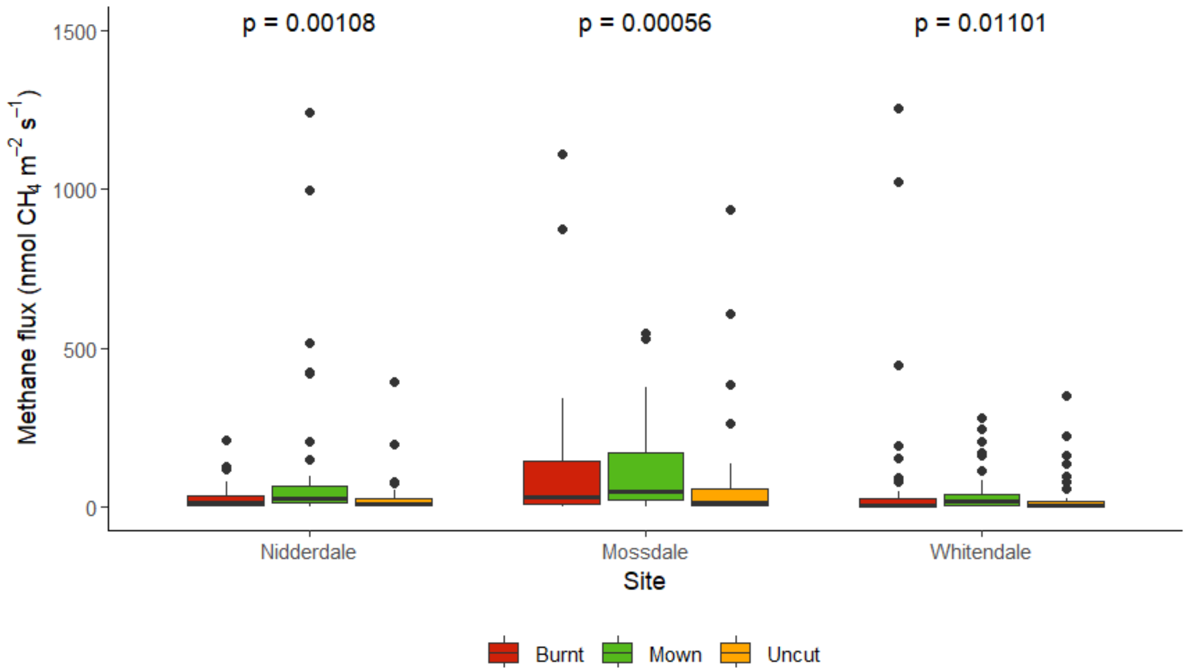


Figure 4.31 Methane fluxes from mesocosm cores from three grouse-managed (burnt, mown, and uncut) blanket bog (Nidderdale, Mossdale, and Whitendale). Outliers are shown beyond the whiskers. KW significant test result shown.

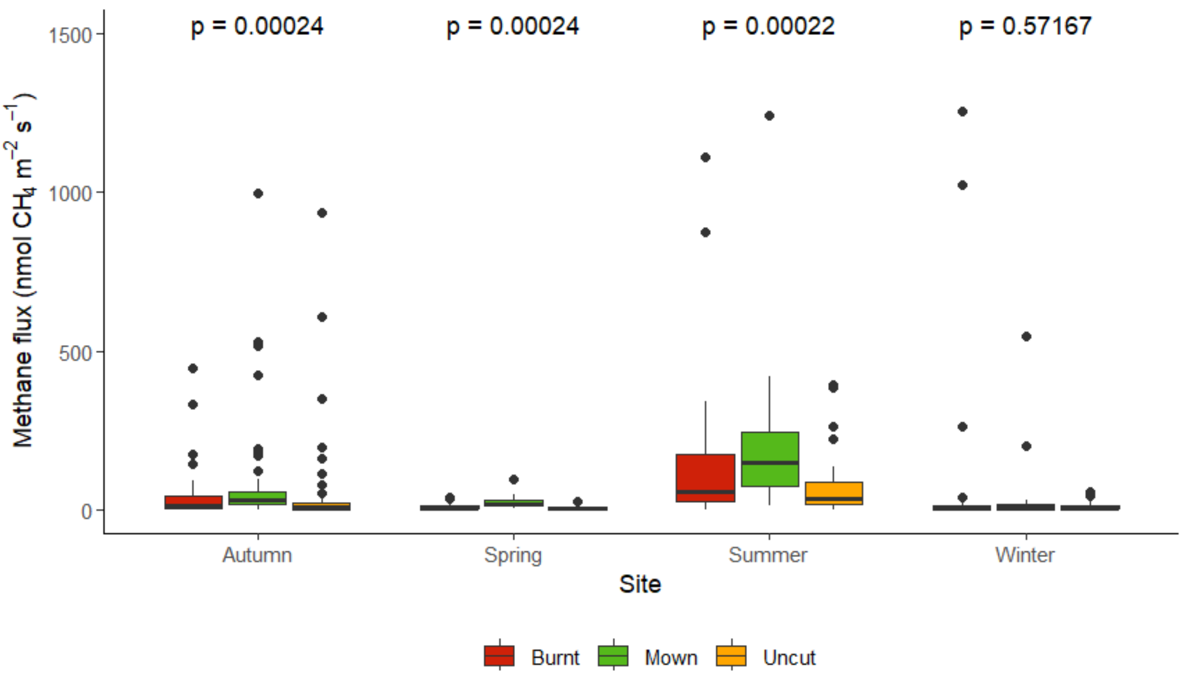


Figure 4.31 Seasonal methane fluxes from mesocosm cores from three grouse-managed (burnt, mown, and uncut) blanket bog. Outliers are shown beyond the whiskers. KW significant test result shown.

Mesocosm core CH_4 fluxes were significantly higher than the fluxes measured in their respective plots in the field (data was log-transformed, $T = -5.05$, $df = 16$, $p < 0.01$). As detailed in Burn (2021),Burn (2021),Burn (2021),Burn (2021), a change factor was calculated by dividing the mesocosm CH_4 fluxes by their respective in-situ field fluxes. Mesocosm fluxes were on average (median) 12 x greater than their respective in-situ fluxes (Table 4.22). The change factor did not differ between site (KW chi-squared = 1.15, df = 2, p = 0.56) nor management (KW chi-squared = 4.35, df = 2, p = 0.11).

Table 4.22 Median methane fluxes (nmol CH_4 m^{-2} s^{-1}) of mesocosm cores from three grouse blanket bog (Nidderdale, Mossdale, and Whitendale) under three management regimes (burnt, mown, and uncut) are their respective in-situ fluxes. The change factor was calculated by dividing mesocosm core flux by in-situ flux for 2019-2022 measurements.

Site	Management	Mesocosm flux	In-situ flux	Change factor
Nidderdale	Burnt	11.93	0.96	12.42
	Mown	23.36	1.24	18.84
	Uncut	7.12	0.16	44.50
Mossdale	Burnt	26.74	1.91	14.00
	Mown	47.74	2.77	17.23
	Uncut	9.38	2.94	3.19
Whitendale	Burnt	3.53	0.41	8.61
	Mown	17.43	1.86	9.37
	Uncut	2.42	1.74	1.39

4.3.6.5 Comparison to CO_2 flux field measurements

Comparison between mesocosm and field GHG measurements show similar trends and differences between management regimes (Figure 4.31). SR_{cut} was higher in the mesocosms compared to the field, and as shown in Section 4.3.6.1, partitioning by cutting roots was less successful. C uptake for Whitendale uncut cores was lower compared to field measurements due to death of core vegetation. Relative humidity was also higher at the mesocosm site compared to the field, due to higher average temperatures.

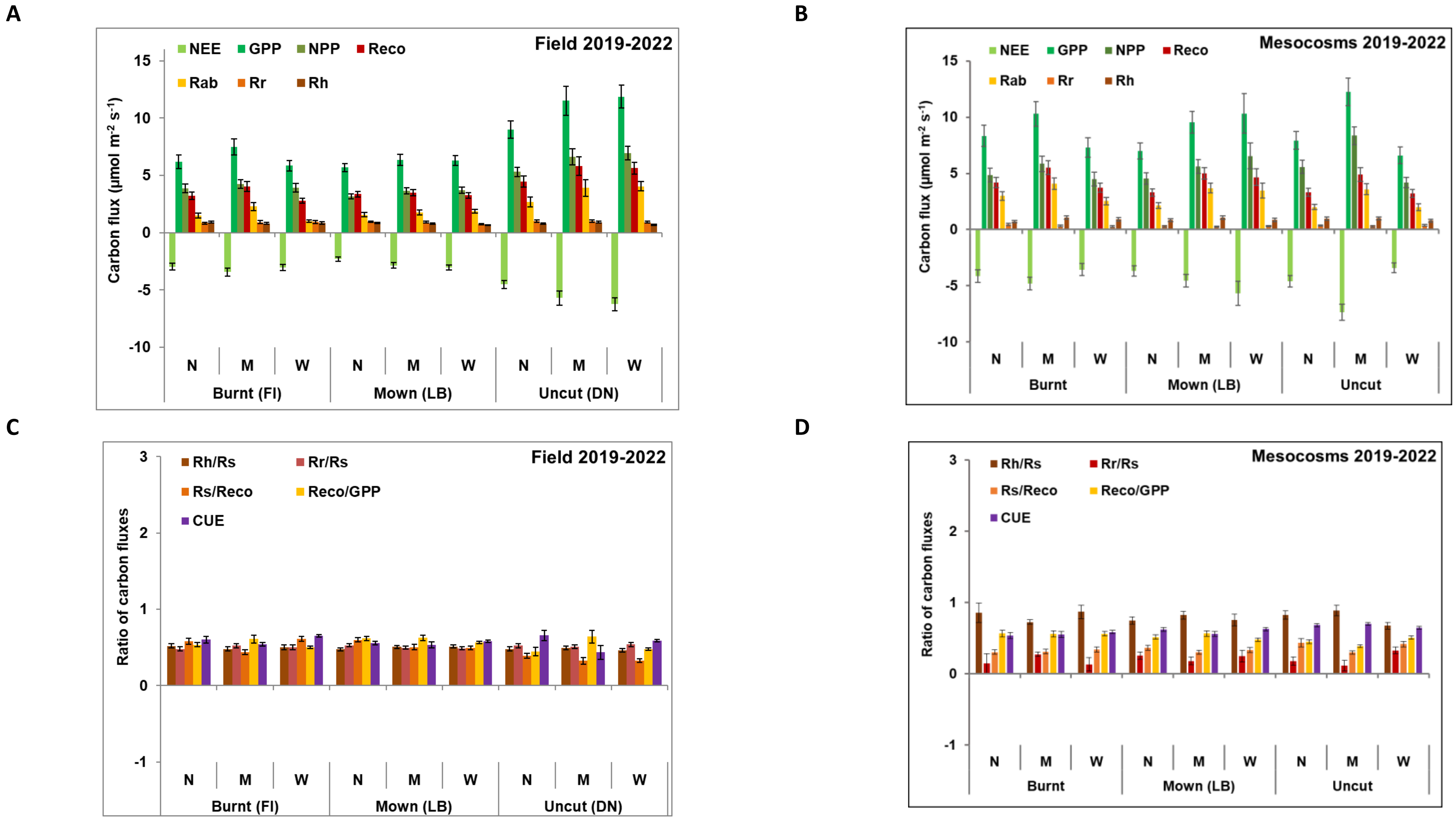


Figure 4.32 Mean carbon gas fluxes of mesocosm cores from three grouse blanket bog (Nidderdale (N), Mossdale (M), and Whitendale (W)) under three management regimes (burnt, mown and uncut). NEE = net ecosystem exchange, GPP = gross primary productivity, NPP = net primary productivity, R_{eco} = ecosystem respiration, R_{ab} = respiration above soil, Rr = root respiration, Rh = relative humidity, CUE = carbon use efficiency. Error bars show standard deviation.

4.3.7 Results summary

Significance test results for water quality and GHG flux between managements, sites, and within site differences as reported in this chapter are summarised in Table 4.23.

Table 4.23 Summary of p values obtained from statistical analysis of differences in key vegetation groups and water quality parameters and gas fluxes (net ecosystem exchange, ecosystem respiration, soil respiration (NEE in full light, R_{eco} in the dark, SR with roots respectively) and methane flux) between site, management regime and within site differences as reported in this chapter. p values in bold indicate a significant difference (significant level $p \leq 0.05$).

	DOC	TbN	$SUVA_{254}$	Hazen	pH	% *C. vulgaris*	% *Sphagnum*	% Sedge	% Brash
Site	p = 0.18	**p < 0.001**	0.53	p = 0.0005	0.78	**p = 0.009**	**p < 0.001**	**p < 0.001**	**p = 0.0004**
Management	P = 0.09	**p < 0.001**	0.57	p = 0.07	0.88	**p = 0.005**	**p < 0.001**	**p < 0.001**	**p < 0.001**
Site * Management	**p = 0.019**	**P = 0.003**	0.85	**p = 0.02**	0.29	**p < 0.001**	**p < 0.001**	**p < 0.001**	**p = 0.001**
	NEE	R_{eco}	SR	Methane					
Site	**p < 0.05**	**p < 0.05**	p = 0.72	**p < 0.01**					
Management	p = 0.08	p > 0.05	p = 0.33	**p < 0.01**					
Site*Management				**p < 0.01**					

4.4 Discussion

The management of UK blanket bog vegetation for red grouse has become a contentious issue (Davies *et al*., 2016), both in the popular press and scientific literature. There are conflicting reports on the effects of management (particularly prescribed heather burning) upon ES (such as drinking water provision and C-storage). This project intended to provide further insight into water quality aspects in relation to heather management coupled with C dynamics from peat soils. Much of the evidence is limited by short-term and Space for Time (SfT) studies, which struggle to account for confounding factors (Ashby and Heinemeyer, 2019). Currently, there is conflicting evidence within the literature with regards to burning and its impacts, and conflicting evidence, and even less is known about the alternatives of cutting or no management (Davies *et al*., 2016; Harper *et al*., 2018). It is important to note that this work is part of a larger, long-term, and more robust Before-After Control-Impact (BACI) field study (Heinemeyer *et al*., 2023), assessing the effects of management, which have been studied further within this thesis via mesocosms taken from the same sites and experimental areas. As such, a comparison to findings in the field requires consideration of different environmental conditions, but different conditions should have affected all mesocosms similarly, allowing exploration of a causal link between management and differences in water quality and C dynamics. This is the first such study to compare intact and fully replicated blanket bog mesocosms to findings from a BACI field experiment on burning, cutting, and no heather management.

4.4.1 Vegetation

C. vulgaris is an ericaceous shrub which dominates much of the UK blanket bog (Noble, 2018) and has been routinely burnt for the management of grouse for game shooting (Grant *et al*., 2012). The dominance of this shrub and its management has been at the center of the upland peatland management debate, with a likely historic burn management and dominance over a considerable time (Davies *et al*., 2016). *C. vulgaris* was the most common dominant vegetation type amongst the blanket bog mesocosm cores, which concurs with site observations (Heinemeyer *et al*., 2019) and the wider literature (e.g., Holden *et al*., 2007). Indicator species analysis (Table 4.3) showed that *C. vulgaris* was significantly associated with uncut cores, which was expected given that management facilitates the removal and subsequent regeneration of *C. vulgaris* shoots (Milligan *et al*., 2018). However, it remains unclear if greater coverage of *C. vulgaris* is a consequence of heather burning (Noble *et al*., 2018b) which has been attributed to changes in hydrological regime (Holden *et al*., 2014) and a greater tolerance for drier conditions than other peatland species (Noble *et al*., 2018), or a result of natural heather dominance (Davies *et al*., 2016; Ashby & Heinemeyer, 2021; Noble *et al*., 2018). Much of the work currently published compared burnt and control plots and did not consider mowing as an alternative management practice (Harper *et al*., 2018) and there seems very little information for a UK blanket bog context except for the Peatland-ES-UK study (Moody and Holden, 2023).

Burning has been repeatedly linked with higher DOC in peatlands (e.g., Yallop and Clutterbuck, 2009). This study found that uncut cores (from historically burnt areas) had the highest mean DOC concentration and showed a positive correlation between *C. vulgaris* cover and DOC concentration. Compared to smaller vegetation, the presence of large *C. vulgaris* plants will lead to an increase in seasonal input of labile plant material into the peat soil due to higher annual biomass production, litter, and root carbon inputs (Ritson *et al*., 2016). Litter in the form of brash was a large proportion of cover for uncut mesocosms, with brash shown to be associated with higher DOC concentrations along with higher NPP. In addition, *C. vulgaris* flowers produce more DOC than other peatland vegetation, and as flowers are a seasonal source of labile OM this could contribute to an elevated DOC concentration during warmer months (Ritson *et al*., 2016) which has been shown by Heinemeyer *et al* (2019). *C. vulgaris* may therefore be problematic from a drinking water treatment perspective due to higher DOC. It also likely has a higher chloroform formation potential (see Chapter 7) compared to *Sphagnum* and *Molinia* (Ritson *et al*., 2016).

Whilst the presence of *C. vulgaris* is desired on UK blanket bog from a grouse-shooting perspective, *Sphagnum* has conservation value and is a known significant contributor to ES such as improving WQ (Armstrong *et al*., 2012) and C accumulation (Clymo and Hayward, 1982). This occurs through the retention of moisture in upper soil layers (Kettridge *et al*., 2015), and acidifying the local environment and slowing microbial decomposition, thus enhancing peat accumulation (Clymo, 1984). However, the concept of peat-forming species and the role of *Sphagnum* versus heather for peat formation is not “either / or” (Ashby & Heinemeyer, 2021). In this work, % *Sphagnum* coverage was significantly higher in uncut cores, suggesting management impacts non-target species, but not necessarily in a negative way over longer time periods, as discussed by Ashby & Heinemeyer (2021). However, burn impacts are complex, with reductions in initial *Sphagnum* cover after burning (Heinemeyer *et al*., 2023) but longer-term recovery bringing likely benefits to *Sphagnum* cover overall (Milligan *et al*., 2018; Ashby & Heinemeyer, 2021). Burning has been shown to cause an initial decline in water table depth (i.e., drier conditions) (Kettridge *et al*., 2015; Heinemeyer *et al*., 2019) associated with an increase in soil water repellency, and exposure of and bare ground causing increased runoff (Nyman *et al*., 2010). However, subsequent recovery has been shown to follow, with water tables being even higher than under older, unmanaged heather (Brown and Holden, 2020; Heinemeyer *et al*., 2023; Worrall *et al*., 2013b). Worrall, *et al* (2007) and Heinemeyer *et al*., (2023) reported higher water tables on 10-year post burn and deeper water tables on unmanaged, old heather plots, which can be attributed to the higher evapotranspiration losses from large vascular plants like *C. vulgaris* – which is expected to result in a long-term decline in net carbon uptake (Heinemeyer *et al*., 2023). Similarly, Milligan *et al* (2018) found that *Sphagnum* was most abundant in most recently burnt plots, which likely relates to increased light levels in an open canopy or the release of substrates and nutrients essential for seed germination and establishment (Clymo, 1973; Bonnett, Ostle and Freeman, 2010). The results reported in this thesis and within the above cited literature suggest that prescribed burning as a tool for promoting *Sphagnum* regrowth is dependent upon the peatland in question, the time scales of management, length of recovery, and that there is unlikely a "one-size fits all" approach to vegetation management with peatland conservation as the overarching aim.

4.4.2 Bulk density

In peatland soils, an increase in BD is seen to reduce water storage and availability, which is particularly problematic for non-vascular plants such as mosses which rely on passive capillary transport (Sagot and Rochefort, 1996). Notably, *Sphagnum* moss growth has been shown to be impeded by higher bulk density (Noble *et al*., 2017). Moreover, changes in BD due to changes in WTD, so called 'bog breathing' has been linked to peatland status (Morton and Heinemeyer, 2019), with more intact/least modified peatlands showing greater flexibility and recovery in BD after drought.

The BD of peat soil samples in this work was comparable with other studies with an average BD of 0.1 g cm^{-3} over at about 0-15 cm depth (Table 4.24). BD of soil from burnt plots was slightly higher at each site compared to mown and uncut plots (Figure 4.4). Fire can cause significant changes to soil hydrological behaviour (Wondzell and King, 2003) and as detailed above, has been reported to increase repellency, thus decreasing infiltration in non-macropore zones (Nyman *et al*., 2010). When this is prolonged, pore collapse may occur, leading to an increase in bulk density and a decline in soil moisture. However, this post-burn increase is not necessarily permanent, and recovery has been stated to be around 20 years if no further burning takes place (Holden *et al.*, 2014). The burning of vegetation also results in the production of charcoal which fills pore space, thus increasing BD (Heinemeyer *et al*., 2018 and Heinemeyer *et al*., 2018) which represents a significant and likely very recalcitrant C store.

Mown cores were initially expected to have higher BD values due to the use of heavy cutting machinery (tractors) which compresses the peat (see Heinemeyer *et al*., 2019). However, mowing may be less detrimental to *Sphagnum* mosses, as brash left over from mowing may retain moisture, thus preventing drying of the peat surface (Morton, 2016). Moreover, Heinemeyer *et al*., (2019) found no lasting plot-level impacts of compaction due to mowing machinery on either BD or peat depth, and in the mesocosms in this study, BD was also not significantly higher in mown plots.

Table 4.24 Reported surface (0-15 cm) bulk density of peatland management studies within the literature.

Bulk density (g cm^{-3})	Notes	Reference
0.10 ± 0.03	Mean BD at 0-15 cm depth from peat soils taken from three blanket bog sites in the Yorkshire Dales National Park, UK.	This study
0.12 ± 0.07	Mean dry bulk density of northern peatland (Northern Europe and America) soil samples.	Loisel *et al* (2014)
0.14 ± 0.03	Mean BD at 0-15 cm depth from peat soils taken from various sites within the Bamford Water Treatment Works (North Derbyshire, UK) catchment.	Crouch and Chandler (2021)
0.06 – 0.15	Range of BD from peat soils in three grouse-managed blanket bogs in the Yorkshire Dales, UK.	Heinemeyer, *et al* (2019)

4.4.3 Soil moisture

SM at the time of mesocosm core collection was shown to be significantly higher in mown plots compared to burnt and uncut plots, but the mean difference was only 5 % and 3 % respectively. SM was expected to be lower in burnt sites, as hydrophobic compounds left following burning form water repellent coatings on soil particle surfaces, and can form interstitial hydrophobic particles (Franco *et al*., 2000), thus preventing infiltration leading to an increase in overland flow and soil erosion (Jiménez-Morillo *et al*., 2017). In mineral soils, the sealing of macropores by ash and fine sediment has been reported to prevent infiltration (Onda *et al*., 2008), thus causing a decline in soil moisture. Holden *et al.* (2014) reported a decline in the role of macropore flow in upper peat layers following burning, which may be linked to macropore collapse due to bare peat being subject to drying (Silins and Rothwell, 1998). However, it is postulated that this is not long-lasting, as removal and degradation of this deposited sediment over time allows for the establishment of macropore networks along with root formation and a return to pre-burn vegetation cover (Holden *et al*., 2014). This is confirmed by raised water tables over time after burning, with the highest WTD reported for plots 10+ years after burning in both the SfT study by Brown *et al*. (2014) and the BACI study by Heinemeyer *et al*. (2023).

Peatland soil chemical processes are largely controlled by water table depth and the depth to anoxic conditions (Ellis *et al*., 2009). Uncut plots had a higher median % coverage *C. vulgaris* which consists of larger plants with a large canopy, which is associated with lower water table depths (Heinemeyer *et al*., 2023). Thus, in the context of ES, it may be beneficial to aim for a heather management regime to maintain conditions (high soil moisture and lower BD) which overall reduces excessive old heather coverage whilst also promoting *Sphagnum* growth.

Fire reduces the size of the critical hydrological buffer that regulates the near-surface moisture content and maintains the low tensions necessary for *Sphagnum* recolonisation (Sherwood *et al*., 2013). On sloped areas of blanket bog, *Sphagnum* is associated with slower overland flow compared to bare and sedge-dominated areas, which can reduce peak flow in rivers, which is important in flooding and soil erosion prevention (Gao *et al*., 2015). Maintaining a high-water table likely promoted establishment of a moss-dominated ground layer within a decade since fire. However, important to note is that peatlands are inherently different in their water holding capacity and thus carbon accumulation, e.g. drier blanket bogs compared to much wetter raised bogs, as shown by Glatzel *et al* (2023).

4.4.4 Carbon:nitrogen ratios

C/N of samples taken from Whitendale were shown to be significantly lower than those from Nidderdale and Mossdale. In peatlands, C:N decreases with depth due to an increasing C loss and higher C:N being associated with plant litter (Leifeld *et al*.,2020; Wang *et al*., 2015). Therefore, it is possible that artificial drainage or mismanagement has led to a decline in water table depth, thus leading to enhanced decomposition in the upper soil layers (Evans *et al*., 2021a). With increased decomposition in peat soils, N accumulates relative to C, as C is lost through mineralisation during OM decomposition as CO_2 or CH_4 (Wang *et al*., 2015a; Leifeld *et al*., 2020). But for blanket bogs, also as a considerable amount of DOC (Heinemeyer *et al*., 2023). This limits overall carbon accumulation compared to wetter (e.g. raised) bogs (Glatzel *et al*., 2023; Wang *et al*., 2015a; Leifeld *et al*., 2020. However, in this work, the GHG flux from peat soils from Whitendale were not significantly higher than the other two sites, suggesting the increased mineralisation and decomposition rates and subsequently GHG emissions are not long lasting.

Peat samples taken from burnt plots had lower C:N ratios compared to mown and uncut plots, but this difference was not significant. As discussed, burning increases the repellency of soil, thus preventing infiltration (Nyman *et al*., 2010) and is therefore associated with a decline in water table depth. However, this effect decreases with time since burn (Worrall *et al*., 2007). Burning therefore increases the depth of the aerobic zone in the peat soil profile (although maybe by only a few centimetres (Heinemeyer *et al*., 2023)), which can lead to enhanced decomposition (Evans *et al*., 2021a) and thus a decline in soil C:N ratios (Wang *et al*., 2015). However, detailed C/N analyses revealed charcoal-related increased carbon content from heather burning (Heinemeyer *et al*., 2018).

4.4.5 Dissolved organic carbon (DOC)

Whilst there are few studies (Worrall *et al*., 2013; Heinemeyer*et al*., 2018) investigating the effects of mowing on DOC, there have been many studies investigating the effects of burning, the majority of which focus on northern UK blanket bog sites (Worrall *et al*.,2007; Clay *et al*., 2010; Clay *et al*., 2012) as well those in Exmoor (e.g., Mills *et al*., 2010). There are reports within the literature that burning increases DOC (Glaves *et al*., 2013) as well as colour (Clay *et al*.,2012; Glaves *et al*., 2013), but these findings are not unanimous (Clay *et al*.,2010). Currently, there is a lack of robust studies with many studies report conflicting findings (Harper *et al*., 2018). Issues include differences in scales (temporal and spatial) and inadequate experimental designs not allowing confounding factors such as vegetation cover or drainage to be resolved (Ashby & Heinemeyer, 2019; 2021).

DOC concentrations in the mesocosm cores was higher than those typically reported in other studies (Table 4.25) with expected seasonal changes as reported in long-term studies (Heinemeyer *et al*., 2019). Porewater DOC concentration is generally higher during periods of low rainfall and drought (Blodau, 2002; Limpens *et al.*, 2008), and due to the lack of through and overland flow in the mesocosms, DOC concentration is somewhat higher than that of field samples, but differences were comparable between sites.

As with the field study (Heinemeyer *et al*., 2023), there were no significant differences between DOC concentrations in porewater between management regimes, but median DOC concentration of burnt cores was higher than mown cores (Table 4.8). Other studies (e.g., Yallop and Clutterbuck, 2009) reported differences between burnt and control plots, but elevated DOC concentrations which have commonly been seen immediately following a burn have been reported as not being long lived (Clay *et al*., 2009; Yallop and Clutterbuck, 2009). Increases in DOC following a burn may be due to the persistence of lipids following the combustion of OM, as these are recalcitrant and hydrophobic (Franco *et al*., 2000) and thus they are not easily degraded or dissolved. Therefore, concentrations of these compounds rapidly increase following a burn. However, due to charges on these molecules, coagulation may occur, thus potentially contributing to the solid peat fraction rather than remaining suspended in the pore water. Burning has also been reported to reduce saturated hydraulic conductivity and macropore flow in upper peat layers (Holden *et al*., 2014) and thus, with lower soil moisture, water movement through peat profile is likely to be slower. This means that more time is permitted for natural coagulation to occur and thus contribute to the peat soil C pool. In addition, burning at the sampled sites took place in early 2013, so any initial effects may no longer be reflected by DOC concentrations.

Table 4.25 Dissolved organic carbon concentrations of soil water reported in similar comparable blanket bog studies within the literature.

Dissolved organic carbon concentration (mg L^{-1})	Measure	Reference
2.95 – 397.98	Maximum and minimum porewater concentrations of mesocosm cores.	This study
5 - 120	Maximum and minimum porewater concentrations taken in-situ from three managed grouse moor blanbket bogs.	Heinemeyer *et al* (2019)
4.06 – 26.08	Maximum and minimum of four-month mean for waters draining from peatland soils in Yorkshire catchments.	Yallop and Clutterbuck, (2009)
5 - 65	Estimated maximum and minimum DOC concentrations of soil water samples in plots of varying times elapsed since last burn. Estimated DOC values taken from figure 3.	Clay *et al* (2009)

Notably, median DOC concentration of uncut cores was higher than in burnt and mown cores, but the difference was only significant compared to mown cores. Consistent with findings in this work, White *et al* (2007) found that in mature (not recently burnt) heather patches, DOC concentration was elevated due to a lower nutrient input (i.e. charred organic matter and cut vegetation) and subsequent lower productivity. There is, therefore, a likely lower turnover of OM leading to accumulation of recalcitrant compounds in pore water. Recalcitrant molecules typically dominate OM (Biasi *et al*., 2005) as more labile C is preferentially utilised by soil biota. This was also reflected in higher DON concentrations which were significantly higher in uncut cores compared to burnt and mown cores. There is low nitrogen availability in blanket bogs (Currey *et al*., 2010), and thus managed vegetation represents an input of nutrients into soils which can increase productivity and thus DOC production.

DOC concentration was strongly linked with dominant vegetation type, with cores dominated by brash having the highest median DOC concentration. As indicated by NMDS and indicator species analysis, brash is most associated with uncut plots, and represents an OM input whereby labile C will be preferentially released from decomposing litter and OM utilised by soil microbes. As expected, *C. vulgaris* cover was significantly associated with uncut cores, and heather cover has been linked with elevated DOC concentrations due to drawdown of the water table and an input of labile litter-derived OM to the soil C pool (Ritson *et al*., 2016), together with likely large amounts of root exudate and litter inputs from a dense fine root mat of heather (Heinemeyer *et al*., 2011; Ritson *et al*., 2016). Correlation analysis indicated that % brash coverage was a significant variable in determining DOC concentration along with % sedge, % *C. vulgaris*, and % *Sphagnum* coverage and was used in the GLM to explain variation in DOC concentration amongst managed cores (Table 4.9). The GLM indicated that % *Sphagnum* and % brash coverage were significant drivers of DOC concentration, along with air temperature which is linked with seasonality (Table 4.10).

Seasonality and thus climate has been strongly associated with peatland DOC concentration and gas fluxes (Heinemeyer, Vallack, *et al*., 2018; Heinemeyer *et al*., 2023). DOC concentration was significantly higher in warmer months, which is reported in the literature (e.g., Heinemeyer *et al*., (2023)) and thus suggests that with climate warming projections, DOC loading in peatland draining waters is likely to increase (Fenner *et al*., 2021). Warmer temperatures can increase decomposition rates of available soil organic matter and soil freeze-thaw cycles have been associated with increased release by disrupting OM aggregates, plant roots, and lysing microbial cells (Tiwari *et al*., 2019). Seasonal variations in DOC production have been associated with temperature and moisture driven changes in the rate of microbial processing of OM (Halliday *et al*., 2012). Higher DOC concentrations have been reported in the summer than in winter (e.g. Heinemeyer *et al*., 2019) although soil solution DOC peaks can occur at any time of year (Evans *et al*., 1996). Fluctuations in soil conditions caused by shorter term weather events (such as episodic freezing, freeze-thaw and drought events) have been shown to affect pore water DOC concentrations (Kaiser *et al*., 2001; Tipping *et al* 1999; Clark *et al*., 2012). Overall, temperature has been identified as the main driver of temporal changes in porewater DOC concentrations; as shown in this study, air temperature was a significant driver of DOC concentrations in GLM modelling (Table 4.9).

UV absorbance is a useful proxy for determining the composition of OM within a water sample at relative ease and low cost and is therefore a powerful tool for water utility companies. Uncut plots had a higher median UV_{254} absorption than mown and burnt plots, although this was only significant compared to mown samples. When corrected for DOC concentration ($SUVA_{254}$), this difference was no longer significant, suggesting the difference in absorbance was due to a higher DOC concentration rather than a larger humic fraction. At all three sites, mown samples had a higher $SUVA_{254}$ than burnt plots; however, this difference was not significant which may be attributed to brash decomposition. As with DOC concentration, hazen of porewaters from uncut plots was higher than mown and burnt plots, yet this was not significant. Lower hazen (and thus colour) is associated with fresh DOC input, as absorbance values from fresh leachates have been shown to be lower than older more degraded DOC, as it is generally dominated by smaller chained, less recalcitrant OM (Beggs and Summers, 2011). Therefore, this suggests that the either the turnover of OM is slower in uncut plots, or other carbon inputs dominate, so the DOC is dominated by more recalcitrant compounds. Whilst this increases colour and thus coagulant demand, these compounds are amenable to coagulation and chemical treatment, and therefore do not represent a significant source of DBP precursors. However, most colour is produced immediately following a burn and then as vegetation recovers, colour production may decrease (Yallop *et al*., 2008). Overall, this suggests that water quality is diminished in unmanaged plots with aging heather cover due to a lower turnover in OM and an accumulation of recalcitrant material. Thus, either vegetation management strategy may be an important tool in improving water quality at the head of catchments. However, this is to be balanced with long-term C storage, which might be more likely to occur in unmanaged or burnt plots (due to charcoal production; (Heinemeyer, Asena, *et al*., 2018). However, a lower water table (e.g. Worrall *et al*., 2013; Heinemeyer *et al*., 2023) and observed decline in net carbon uptake (Heinemeyer *et al*., 2023) might suggest otherwise.

Other wavelengths were investigated using UV broad spectrum data, but no significant differences were observed between sites or managements for key wavelengths reported in the literature (e.g., UV_{280} and UV_{365}). Wavelength ratios were also investigated (Table 4.14) and no significant differences were shown, suggesting that whilst DOC concentration differs between managements, the general composition of the DOC does not. Thus, WQ can be improved by management of peatland vegetation through the reduction of soil water OM and carbon compound loads.

4.4.6 pH

Blanket bog soil generally has a pH of ~4 and thus measurements taken during this study are typical of those generally reported (Brown *et al*., 2014; Heinemeyer *et al*., 2023). pH is an important soil characteristic, given that pH controls DOC solubility, with acidic and saturated soil conditions in peatland ecosystems inhibiting OM decomposition (Holden *et al*., 2012). pH is also linked to C cycling (Heinemeyer *et al*., 2019) and CH_4 emissions (Abdalla *et al*., 2016). Positive correlations between DOC solubility and pH have been reported (Fenner *et al*., 2005; Lofts *et al*., 2001; Lumsdon *et al* 2005).

It has been claimed that burning alters peat soil pH with some studies reporting a decline in pH following a burn (Clay *et al*., 2012; Brown *et al*., 2014) and others reporting an increase (Forgeard and Frenott, 1996). There were no significant differences in pH between management regime or site in this study. GLM modelling indicated that pH was not a significant driver of variances in DOC concentration between management regime, but pH and DOC were significantly negatively correlated (Table 4.17). pH differed significantly with collection month, which is likely due to soil moisture levels (Clark *et al*., 2012) and was significantly negatively correlated with soil temperature. This is likely to be problematic under projected climate warming scenarios, with lower porewater pH leading to higher DOC solubility. This therefore represents a mechanism by which soil C stocks may become destabilised.

4.4.7 Conductivity

Conductivity of peatland porewaters is significantly lower than that of mineral soils due to low nutrient levels. Porewaters from mown cores had the lowest median conductivity, but this was not significant. It was hypothesised that porewaters from burnt and mown cores may have higher conductivity values due to the input of fresh litter post-management in the form of brash and/or plant residues, but this was not the case. The impacts of management upon conductivity in peat soils is not widely discussed within the literature, although Worrall *et al*. (2007) reported a decline in conductivity on burnt plots compared to unburnt plots. In blanket bogs, an increase in conductivity may represent an input of elemental nutrients, perhaps from atmospheric deposition and/or vegetation, litter, and ash inputs. A significant difference between managements could therefore represent differences in nutrient concentrations which could affect primary productivity and thus gaseous C balance. However, sampling might need to be done at the very surface to capture any small differences, which would quickly be diluted by a larger peat volume.

4.4.8 Gas Fluxes

Peatlands offer a unique opportunity in mitigating rising GHGs and climate change due to their ability to sequester large amounts of C long-term (Freeman *et al*.,2012). However, this process is slow and thus limited over shorter time scales, so currently the key importance is in preventing carbon losses from eroding or drained peat. Understanding peat gaseous fluxes can give an indication of whether a peatland is acting as a carbon source or sink, so understanding links with vegetation can permit management to facilitate the suppression of OM decomposition (Dunn *et al*., 2016).

It is well acknowledged that hydrological conditions have a significant impact upon the C balance of peatlands (Maljanen *et al*., 2010), which are affected by overlying vegetation community composition. Uncut (i.e., unmanaged) cores were significantly associated with *C. vulgaris*, which as a dense-rooting species (Heinemeyer *et al*., 2011) is known to cause water-table drawdown (Heinemeyer *et al*., 2023). Lower water tables are associated with CO_2 net emissions due to increased OM decomposition rats (Maljanen *et al*., 2010) and this has been linked to a decline in NEE and NECBs for the same sites (Heinemeyer *et al*., 2023). The observed threshold between C sink/source of about 12 cm was surprisingly similar to that reported by Evans *et al* (2021).

Lower water tables are associated with net emission of CO_2 whilst higher water tables lead to an increase in CH_4 emissions (Haddaway *et al*., 2014). In water-saturated soils, C is emitted as $CH_4$and following a decline in water table depth due to an increase in soil oxygen availability and thus, oxidation of CH_4 by methanotrophs (Abdalla *et al*., 2016; Dunn *et al*., 2016). However, as noted by Frolking *et al*. (2006), the long-term sequestration of C which occurs under saturated conditions outweighs the warming effects of CH_4 due to the comparatively shorter lifetime of the latter (Evans *et al*.,2016), at least when calculated for a 100-year time frame.

Mesocosm CO_2 fluxes were comparable to those measured in the field (Figure 4.31), as reported by Heinemeyer *et al*., 2023) despite differences in average temperature. Whilst there were no overall significant differences in SR or NEE between management regime, uncut cores at Mossdale (the best heather condition), showed highest NEE C uptake. Moreover, mown cores had significantly higher CH_4 fluxes than burnt and uncut cores, comparable to field observations (Heinemeyer *et al*., 2023), likely due to higher sedge coverage. CH_4 fluxes measured in the mesocosms were significantly higher compared to measurements taken from their in-field counterparts, and these differences were consistent across sites and management regime. This may be due to the 3°C warmer annual mean temperatures in York (about 15 m asl) where the mesocosms were stored compared to in-situ conditions in the uplands (about 400 m asl). However, average conditions for light and mesocosm water tables in York were within range of those observed at the field sites. Notably, similarly high CH_4 fluxes (mean fluxes were 9.01 ± 4.68, 12.74 ± 6.19, and 31.88 ± 16.68 for burnt, mown, and uncut plots respectively) were measured in the field during and after a warm and wet period in 2014 during 2015-2017 (Heinemeyer *et al*., 2019). However, the mesocosms were kept wet throughout 2019 (water table depth = -5 cm). Therefore, CH_4 emissions were likely stimulated by warmer and wetter conditions, which agrees with higher CH_4 field emissions during 2015-2017 (Heinemeyer *et al*., 2023). GLM modelling showed that vegetation coverage was not a significant control on variation in CH_4 fluxes, suggesting that site specific and/or management induced physical characteristics are more significant determinants on fluxes. CH_4 emissions in peatlands are controlled largely by water table depth, and thus anoxia, temperature, pH, and nutrient availability (Basiliko *et al*., 2003; Abdalla *et al*., 2016). Unmanaged cores were significantly associated with *C. vulgaris*, leading to increased uptake and evapotranspiration loss of soil water and thus a decline in water table depth.

Whilst there were no significant differences in NEE between management regime, median NEE was lowest in uncut cores. This is likely due to the large biomass of older, uncut *C. vulgaris* plants. Managed plots on blanket bog was shown to be a C source following management (Heinemeyer *et al*., 2018b), with recovery back to net C sink was quicker on mown plots which may be due to wetter soil conditions (Heinemeyer *et al*., 2023). NEE was significantly lower in Mossdale cores which likely due to in-field higher annual precipitation which reduces SR due to a higher water table as lower water table depths have been associated with positive net CO_2 emissions, and thus increased R_{eco} and SR (Freeman *et al*., 1993; Haddaway *et al*., 2014). Hydrological conditions have a significant impact on the C balance of peatlands (Evans *et al*., 2021; Glatzel *et al*., 2023) and the CO_2 balances of individual peatlands differ in their sensitivity to climate variability (Maljanen *et al*., 2010).

4.5 Conclusion

This is the first experiment to directly compare key carbon and GHG flux and WQ measurements from a field experiment comparing uncut, burnt, and mown heather-dominated blanket bog areas to paired peat mesocosms. It was shown that key environmental conditions were maintained near average field conditions, with good consistency for light and water tables but less so for temperature. However, this confirmed a direct comparison is possible and meaningful, and therefore provides a new approach for experimentally studying peat ecosystems. Using parameters of WQ for soil porewaters, ecosystem carbon fluxes, and soil GHG emissions from mesocosm cores taken from managed blanket bog peatlands, this study has assessed the impacts of management on WQ and soil gaseous fluxes under comparable conditions to those in the field. Nearly all investigated parameters showed close similarity between observations made in mesocosm and field locations; where they do not align (i.e., CH_4 and R_{eco}), these could be linked to differences in temperature (i.e. warmer in York than in the field) and plant biomass (i.e. heather in uncut treatments).

Hypothesis 1 stated that mowing would benefit water quality which was shown to be incorrect. For the water quality parameters investigated, there was no significant difference between management regimes. Management was shown to lower DOC concentrations and UV absorbance and thus improving water quality. There were some within site differences in water quality parameters which indicates that management should be tailored to specific sites. Hypothesis 2 was shown to be correct. Significant differences in water quality were shown between cores dominated by different vegetation groups and seasons (linked to temperature and water table depth). This was due to vegetation soil inputs and the introduction of oxygen to the previously anoxic parts of the peat column.

Unsurprisingly, *C. vulgaris* was most significantly associated with unmanaged cores along with *Sphagnum*, which, as uncut areas were previously burnt, suggests that management does not necessarily cause a negative long-term impact. Mown cores had significantly higher CH_4 fluxes which was attributed to higher coverage of sedge along and higher soil moisture. However, from a WQ perspective, peatland management reduces DOC loading in porewaters compared to no management (i.e., uncut cores). Management may therefore be beneficial to water treatment given that there is a lower DBP precursor load prior to removal via coagulation. With regards to the recommended management strategy, there were no significant differences in WQ parameters between burning and mowing, but mown plots had a significantly higher CH_4 flux. This was possibly due to a higher water table, so mown plots may be associated with higher long-term C sequestration rates. Therefore, mowing may be a suitable alternative to prescribed burning long-term, especially for drier sites. It is important to acknowledge that mowing is not suitable on all blanket bogs and has negative impacts on micro-topography (Heinemeyer *et al*., 2019). Therefore, its suitability depends upon site specific features such as topography and slope. UV_{abs} analysis indicated no difference between the composition of DOC between managements, and whilst there were differences in some UV_{abs} between waters from under different managements, SUVA indicated that these differences were likely due to different DOC loads, rather than the composition of DOC.

GHG fluxes were shown to be significantly correlated to temperature which has implications for blanket bog as a C sink in the context of climate change. Over this study, median NEE for all sites and managements was negative. Where cores were dominated by older, taller *C. vulgaris*, NEE was more negative which is beneficial for C sequestration but also linked with lower water quality. Mown cores had significantly higher CH_4 fluxes likely due to increased soil moisture, and where brash was left, there was an improvement in water quality. This suggests that where management may reduce the magnitude of gaseous C sources, this may be accompanied by a decline in water quality. Therefore, the appropriate management regime may depend upon which ES is a priority.

5 Effects of habitat restoration on grouse-moor blanket bog soil parameters and carbon dynamics

5.1 Chapter summary

Many UK blanket bogs have become degraded due to historical management, atmospheric pollution, and climate warming. Consequently, there has been an upsurge in restoration projects focussing on re-establishing a desirable vegetation community (increased *Sphagnum* cover) and raising water tables; however, project success is not consistently reported within the literature. Therefore, this study aimed to assess the impacts of restoration on blanket bog ecosystem services delivery. Seasonal porewater collections and GHG flux measurements were taken from mesocosm cores from three regions of blanket bog of degradation, restored, and intact status. Porewaters from intact cores had a higher DOC load and colour which indicated that whilst coagulant demand in drinking water treatment would be greater, the DOC is more amenable to treatment. Samples from Exmoor cores showed significant differences compared to other sites irrespective of restoration status which is likely due to a high *Molinia* grass coverage. Intact cores had greater C uptake (< net ecosystem exchange and ecosystem respiration) compared with degraded cores however this was due The Peak District cores which were characterised by 100% bare exposed peat. As water table depth and temperature were significantly correlated, it is difficult to establish which exerted more control, and it is likely both were significant drivers of differences in both water quality and GHG fluxes. These findings indicate that restoration success is dependent upon overlying vegetation community and site-specific features. Monitoring over longer time periods (> 10 years) is recommended to assess restoration success.

5.2 Introduction

UK blanket bog is a source of both resources (i.e., peat as fuel) and land (for both forestry and agriculture) and have thus, been exploited over many centuries (Gorham and Rochefort, 2003). Many UK peatlands have become degraded through both direct (i..e, mismanagement) and indirect (e.g., atmospheric pollution, increases in GHG emissions and subsequent climate warming) mechanisms (Rosenburgh, 2015). Consequently, UK peatland coverage is estimated to have declined by 44 % between the 1940s and 1980s (Van Der *et al*., 2011), with approximately 2,962,622 ha remaining, mostly in a modified or degraded state and only about 23% classified as near-natural (Artz *et al*., 2019). Consequently, many UK blanket bogs are now C sources due to drainage, exposure of bare peat, and changes in vegetation coverage, thus exacerbating the climate emergency (Leifield *et al*., 2019; Loisel *et al*., 2021).

In more recent times, peatland restoration has seen a global upsurge due to its potential to protect and restoration ecosystem services (Gatis *et al*., 2023) as drinking water provisioning (Williamson *et al*., 2020) C storage (Wilson *et al*., 2011a), and biodiversity (Heinemeyer *et al*., 2023). Mechanisms by which this is undertaken include ditch blocking and subsequent rewetting, and the planting of 'more desirable' vegetation such as *Sphagnum.* However, its success is not consistently reported within the literature. A large issue with the monitoring of restoration is that its success has been judged on relatively short time scales. Subsequently, periods of restoration have been too short to enable the transition back to 'fully functioning peatland' – ie., to a state that is comparable to 'intact' peatlands elsewhere (Gorham and Rochefort, 2003) especially given that the recovery of 'active' blanket bog vegetation is expected to take between 15 to 20 years (Rosenburgh, 2015). Therefore, longer term monitoring (i.e., 10-20 years – see Heinemeyer *et al*., (2023)) is necessary to determine recovery projection and thus success. Moreover, many peatland studies are space for time studies, where confounding factors are difficult to be considered separately from impacts from management or restoration aspects. Controlled mesocosm studies offer an opportunity to take studies from various locations and keep them under similar environmental conditions, to limit the impacts of climatic and hydrological differences.

Considering this, the aims of this investigation were to assess - in a controlled mesocosm study - how differences in habitat condition or restoration status impact ecosystem service delivery (specifically water quality (in the context of drinking water treatment), C storage, and GHG emissions), and if any differences observed in mesocosm peat cores could be suitable as a measure of recovery of UK blanket bogs. Therefore, the overarching research question for this chapter was '*Is blanket bog restoration beneficial to water quality, C sequestration, and the reduction of GHG emissions?'.*

The hypotheses tested were as follows:

I. Water quality is best in intact blanket bog cores and decreases from restored to degraded cores.

II. Degraded cores will act as a C source whilst intact cores will act as C sinks but with a strong influence by vegetation cover.

III. Vegetation and water table depth will be the most significant factors affecting water quality, C dynamics, and greenhouse gas emissions in mesocosm cores whilst they are kept under similar environmental conditions.

5.3 Results

5.3.1 Vegetation

A NMDS (R package “vegan”, Oksanen *et al.*, 2022) (Figure 5.1) was performed on vegetation survey data (stress = 0.16) showing vegetation community composition differed significantly between sites and restoration status’ (RSs) (ANOSIM R stat = 0.21 and 0.43, significance $p < 0.01$ with 9.9 K permutations respectively). Indicator species analysis (R package “indicspecies”, Cáceres *et al.*, 2022) identified vegetation species significantly associated with RS (Table 5.2). *Sphagnum* was significantly associated with intact cores and coverage was significantly different between intact and all other RSs (KW chi-squared = 48.034, df = 3, $p < 0.001$, post-hoc $p < 0.001$; Figure 5.2). In addition, *Sphagnum* was also significantly associated with Scottish cores (Indicator species analysis stat = 0.537, p = 0.001) which had the coldest and wettest climate of those sites in this study. Bare ground was most significantly associated with degraded cores which is shown in Figure 5.2 where the degraded ellipsis is pulled in the negative direction by NMDS 1. Bare peat % coverage was significantly higher on degraded cores compared with other RSs (Figure 5.3) and was also significantly associated with cores from the Peak District (Table 5.3).

Table 5.1 Indicator analysis (using R stats package “indicspecies”, Cáceres *et al.*, 2022) results showing key vegetation or cover groups significantly associated ($p < 0.05$) with each restoration status (10- and 5-years post restoration, intact, and degraded). Number of iterations = 9999.

	Stat	P value
10Y		
Brash	0.304	0.0001
Herb	0.179	0.0083
5Y		
Calluna vulgaris	0.358	0.0001
Degraded		
Bare	0.634	< 0.01
Lichen	0.258	< 0.01
Intact		
Sphagnum spp.	0.390	< 0.01
Sedge	0.378	< 0.01

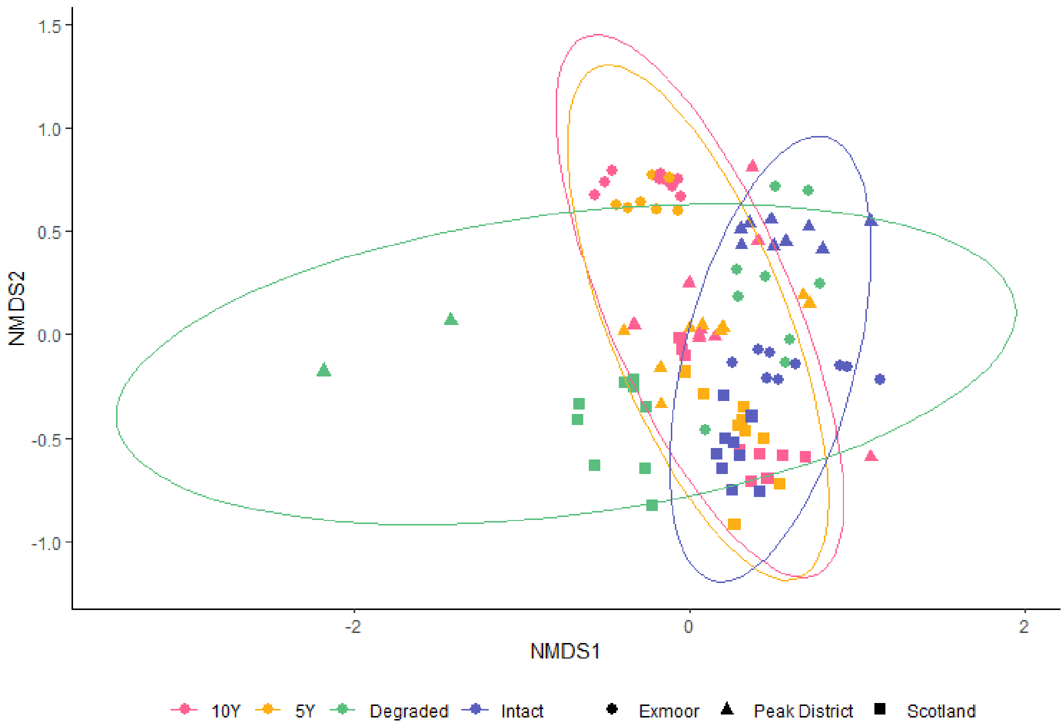


Figure 5.1 NMDS of vegetation groups of mesocosm central cores from blanket bog in three regions (Exmoor, the Peak District, and Scotland) classified by restoration status (10- and 5-years post restoration, intact, and degraded) in the UK. Ellipse show grouping of cores under the same restoration status.

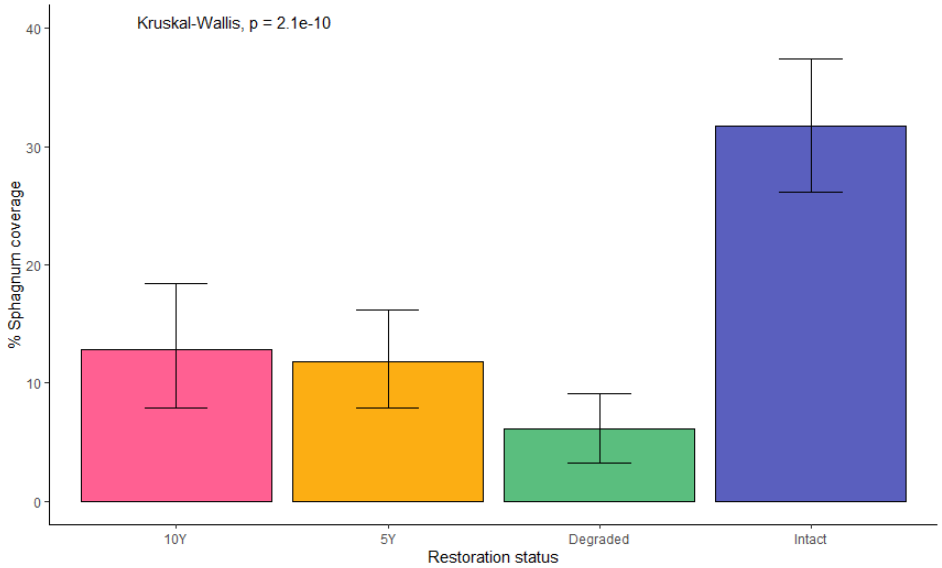


Figure 5.2 Mean % Sphagnum coverage of peatland mesocosm cores taken from three regions of blanket bog in the UK (Exmoor, the Peak District, and Scotland), classified by restoration status (10- and 5-years post restoration, degraded, and intact). Error bars show standard deviation. Significance testing result shown.

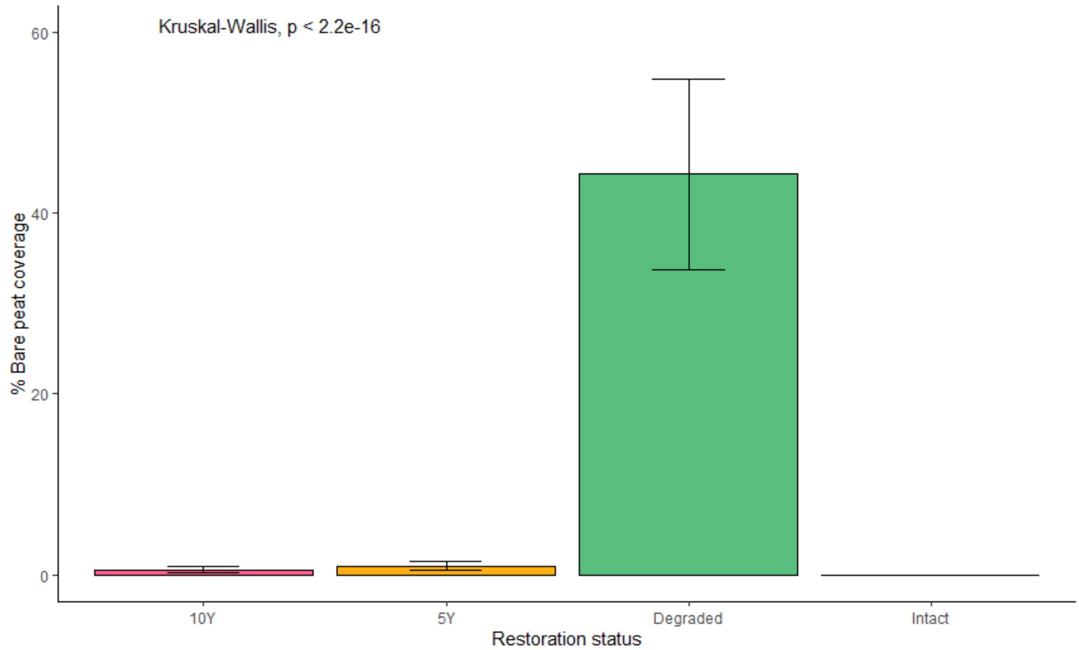


Figure 5.3 Mean % bare peat coverage of peatland mesocosm cores taken from three regions of blanket bog in the UK (Exmoor, the Peak District, and Scotland), classified by restoration status (10- and 5-years post restoration, degraded, and intact). Error bars show standard deviation. Significance testing result shown.

Table 5.2 Indicator analysis (using R stats package "indicspecies", Cáceres *et al*., 2022) results showing key vegetation or cover groups significantly associated ($p < 0.05$) with each region (Exmoor, the Peak District, and Exmoor). Number of iterations = 9999.

	Stat	P value
Exmoor		
Grass	0.802	< 0.01
Peak District		
Bare	0.322	< 0.01
Sedge	0.263	< 0.01
Other moss	0.482	< 0.01
C. vulgaris	0.503	< 0.01
Scotland		
Sphagnum	0.537	0.0001
Lichen	0.253	0.0001
C. vulgaris	0.503	< 0.01

5.3.2 Soil analysis

The following results refer to peat soil samples which were collected ~ 10 cm below the peat surface alongside the mesocosm cores in January and February 2019. 35 soil samples were analysed.

5.3.2.1 Bulk Density

BD ranged from 0.016 to 0.17 g cm^{-3} with a median of 0.09 g cm^{-3} and a mean of 0.10 ± 0.03 g cm^{-3}. BD did not differ significantly between region (ANOVA, F = 3.016, df = 3, p = 0.188) but did between RS (F = 3.016, df = 3, p = 0.045). Post-hoc testing indicated this difference was only significant between degraded and 5Y samples. There were no within region differences between RS however in samples from Exmoor and the Peak District, degraded samples had a higher median BD compared to restored samples. This was not the case for samples taken from Scottish blanket bog (Figure 5.4).

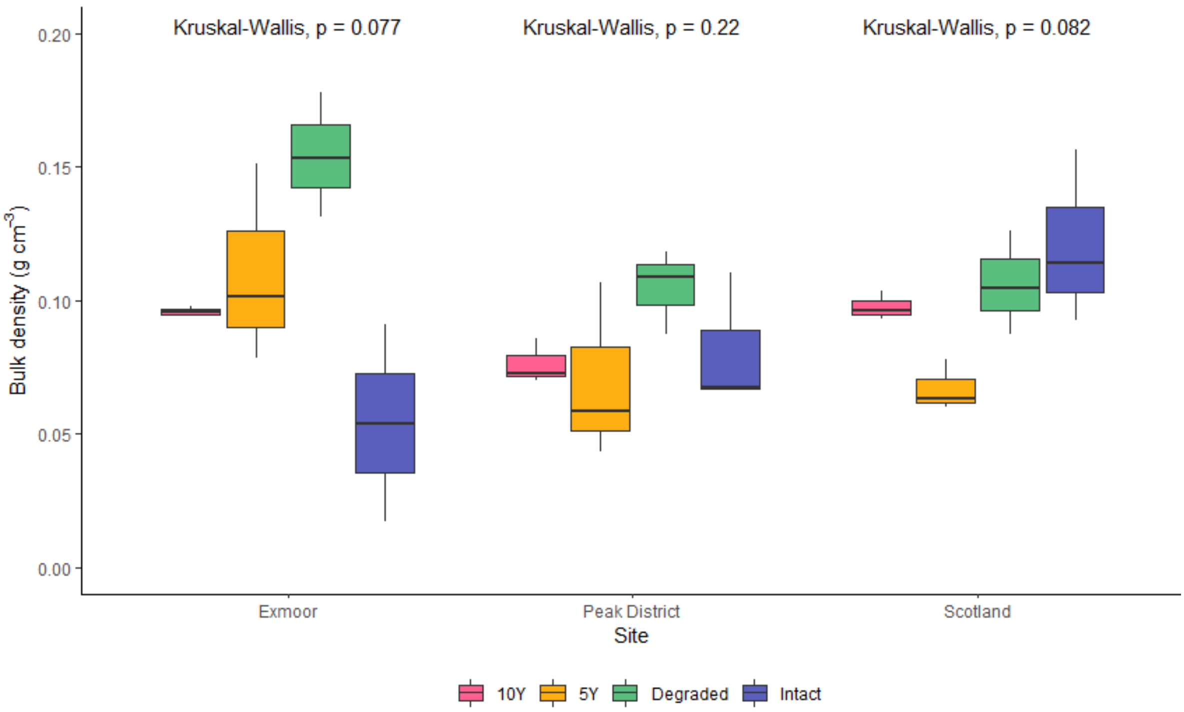


Figure 5.4 Bulk density (g cm^{-3}) of soil samples taken alongside mesocosm cores from three UK regions of blanket bog (Exmoor, the Peak District, and Scotland) classified under 4 different restoration status' (10- and 5-year post restoration, intact, and degraded) . Significance testing results for within region differences shown.

5.3.2.2 Soil moisture

SM ranged from 75.06 to 96.94 % with a median of 88.54 % and a mean of 88.33 ± 4.18 %. SM was compared for within site differences only as it is highly variable depending on weather conditions and soil samples were collected within ~ 30 days. There were no significant within site differences (Figure 5.5) however, intact, and restored samples had a higher soil moisture compared to degraded samples at all sites. SM and BD were significantly correlated ($R = -0.63$, $p < 0.01$).

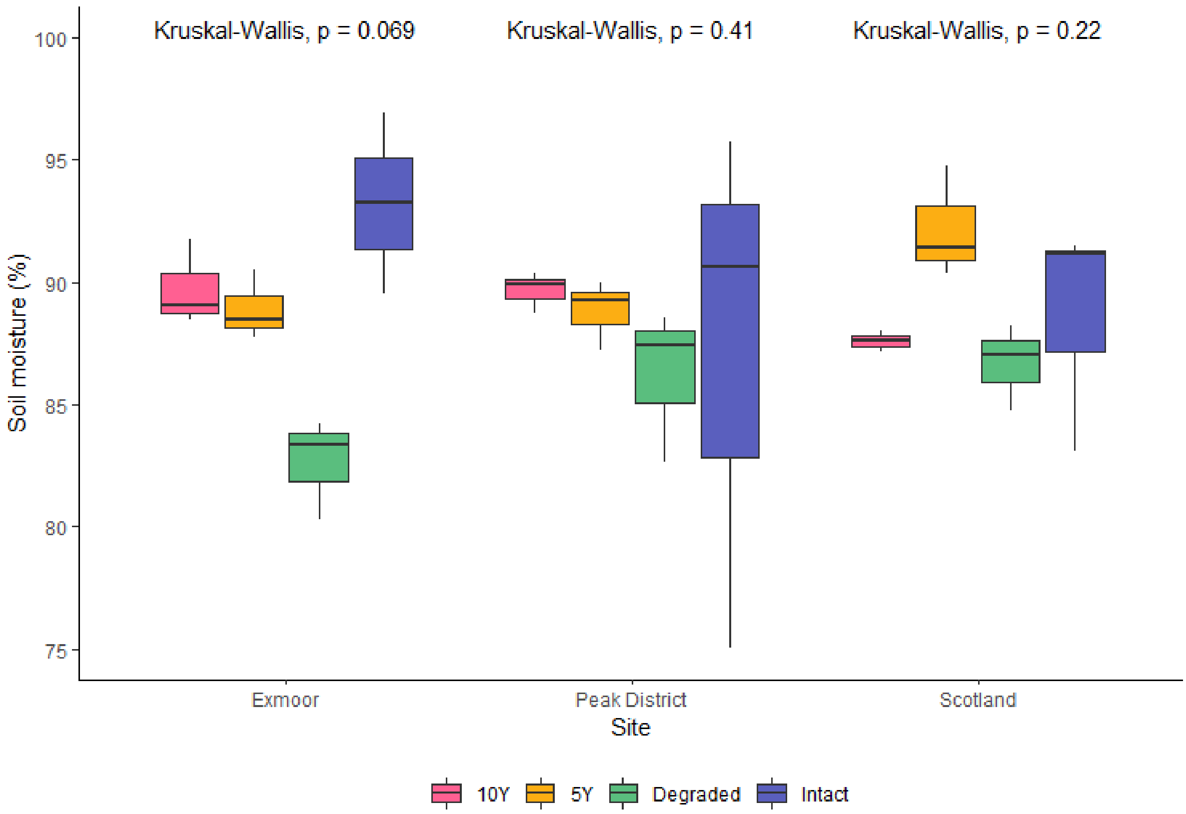


Figure 5.5 Soil moisture (%) of soil samples taken alongside mesocosm cores from three UK regions of blanket bog (Exmoor, the Peak District, and Scotland) classified under 4 different restoration status' (10- and 5-year post restoration, intact, and degraded) . Significance testing results for within region differences shown.

5.3.2.3 Carbon:nitrogen ratio

C:N ranged from 11.42 to 63.87 with a median of 26.44 and a mean of 30.85 ± 15.12. There were no significant differences in C:N between RSs but there were significant differences between sites (KW chi-squared = 16.221, df = 3, $p < 0.001$, post-hoc $p < 0.05$). Samples from the Peak District had the highest median C:N of 51.15 compared to Exmoor which had the lowest of 18.73. Significant within site differences were found between RS in Peak District samples with intact having the lowest median

C:N and 10Y having the highest. In the Scotland sample set, degraded samples had the highest C:N and intact samples the lowest however, this difference was not significant (Figure 5.6).

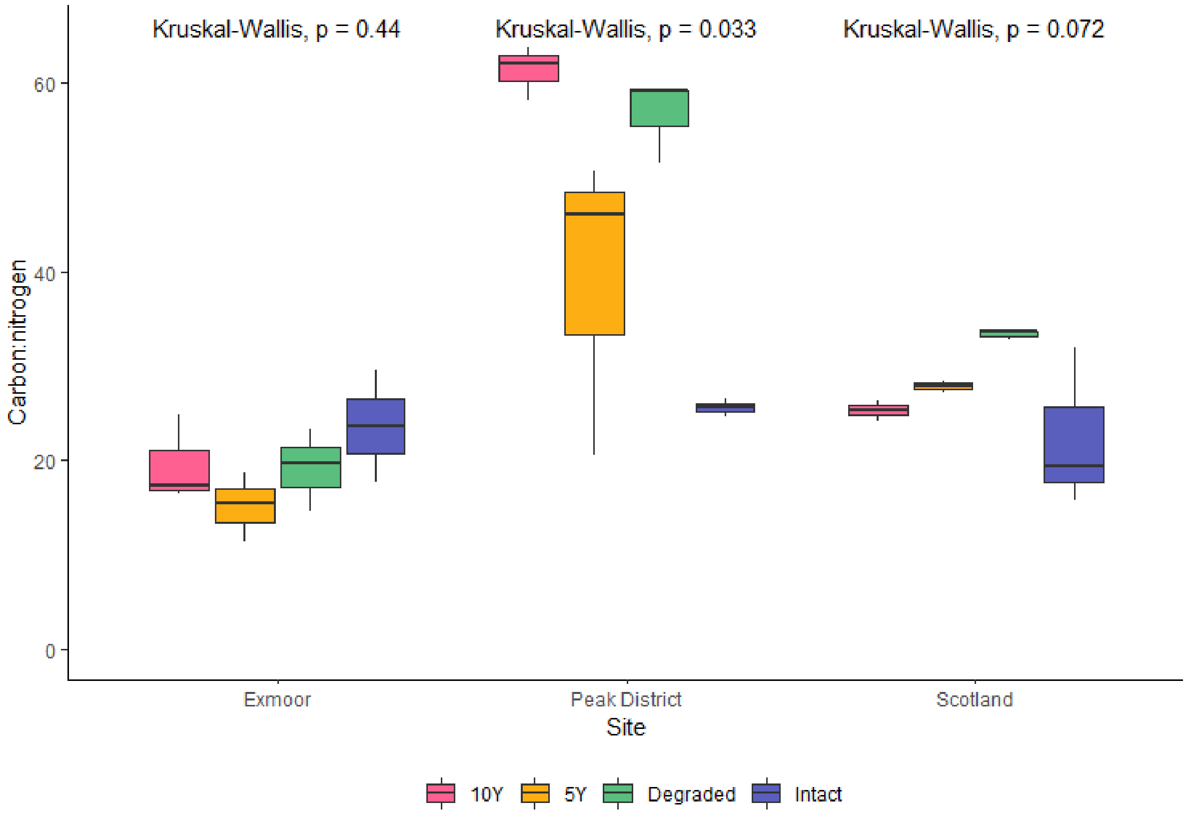


Figure 5.6 Carbon:nitrogen ratio of soil samples taken alongside mesocosm cores from three UK regions of blanket bog (Exmoor, the Peak District, and Scotland) classified under 4 different restoration status' (10- and 5- year post restoration, intact (I), and degraded (D)). Significance testing results for within region differences shown.

5.3.2.4 Soil % organic carbon

Soil % organic carbon (% C_{org}) ranged from 36.51 to 73.20 % with a median of 49.60 % and a mean of 50.12 ± 4.99 %. Scotland had the highest median % C_{org} of 51.35 % and Exmoor the lowest of 48.64 % which was found to be a significant difference (KW chi-squared = 6.14, df = 2, p = 0.04, post-hoc p = 0.036) despite there being a difference of only 2.71 %. 10Y had the highest median % C of 50.97 % compared to intact samples which had the lowest median % C_{org} of 49.58 and this difference was not significant. No within site differences were reported (Figure 5.7).

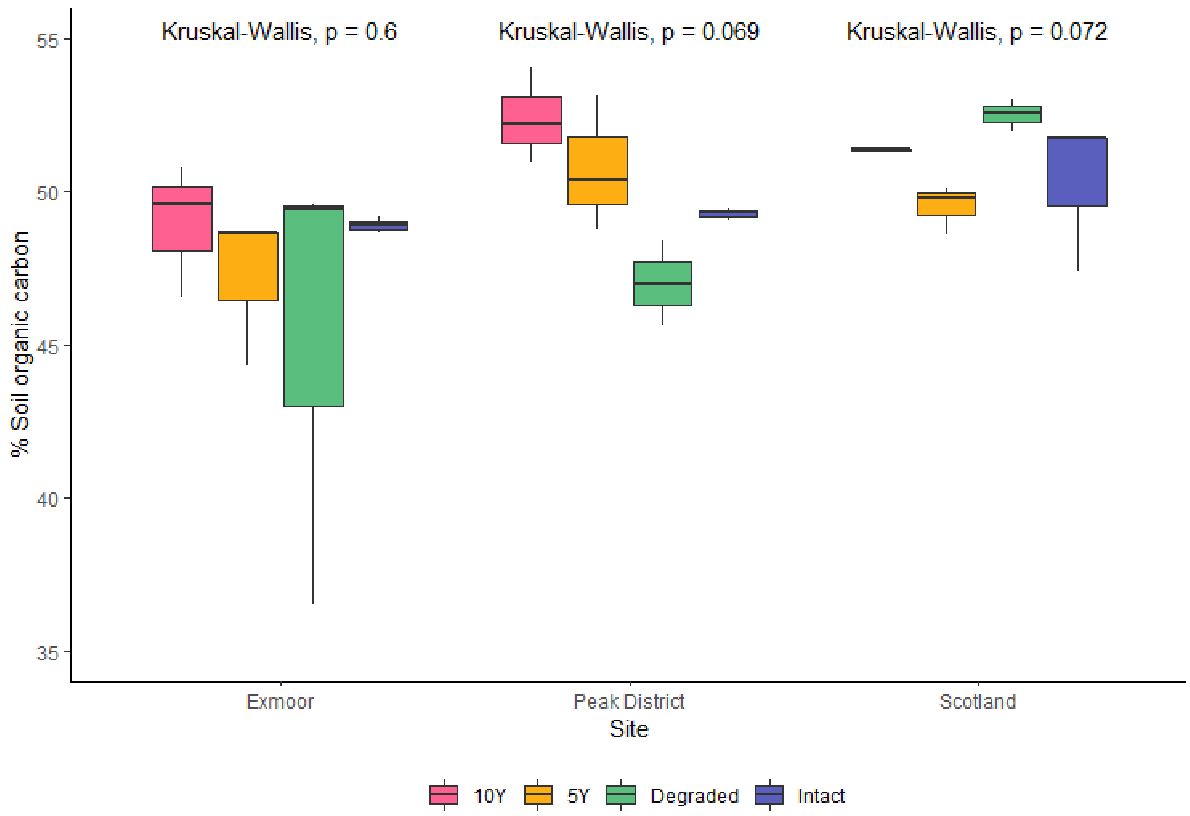


Figure 5.7 % soil organic carbon of peat samples taken alongside mesocosm cores from three UK regions of blanket bog (Exmoor, the Peak District, and Scotland) classified under 4 different restoration status' (10- and 5-year post restoration, intact (I), and degraded (D). Significance testing results for within region differences shown.

5.3.2.5 Linking soil quality parameters to environmental conditions, restoration status and region

A NMDS was performed to determine if region or RS had a significant impact on soil quality parameters (i.e., bulk density, soil moisture, % C_{org}, and C:N) and to determine likely drivers of differences in soil quality parameters in restored-degraded sites. RS and site were used to center the scores for the NMDS, and environmental parameters were used as vectors (Table 5.3). NMDS (Figure 5.8) indicated that longitude, % moss, grass, and bare ground coverage, and elevation are likely significant drivers in differences in soil parameters. ANOSIM analysis indicated that based on the groupings in the NMDS, soil parameters did not differ significantly on the basis of RS (ANOSIM R = 0.03, p = 0.19), however, they did differ significantly by site (ANOSIM R = 0.34, p = 0.001).

Table 5.3 Centroids of factors (blanket bog site (Exmoor, the Peak District, and Scotland) and restoration status (10- and 5-year post restoration, intact, and degraded)) for non-metric multidimensional scaling analysis (NMDS) to determine likely drivers of differences in soil quality parameters (bulk density, soil moisture, % C_{org}, and C:N). Significant drivers in **bold**.

		NMDS1	NMDS2
Site	Scotland	-0.12	-0.02
	Peak District	0.07	0.02
	Exmoor	-0.07	-0.02
Restoration status	10Y	0.02	0.005
	5Y	-0.002	-0.03
	Degraded	-0.003	0.06
	Intact	-0.02	-0.03
Goodness of fit			
	R^2	Pr (>r)	
Site	0.35	**0.001**	
Treatment	0.15	0.12	

Table 5.4 Non-metric multidimensional scaling analysis (NMDS) R^2 and probability scores for vectors used in NMDS analysis for the factors relating to soil quality parameters (bulk density, soil moisture, % C_{org}, and C:N). Parameters with significant p values are indicated in **bold**.

Environmental parameter	NMDS1	NMDS2	R^2	Pr (>r)
% Calluna vulgaris	0.99	-0.16	0.09	0.21
% Moss	**0.97**	**-0.25**	**0.18**	**0.049**
% Sedge	0.89	-0.45	0.05	0.47
% Bare ground	**0.61**	**0.79**	**0.26**	**0.027**
% Grass	**-0.99**	**-0.13**	**0.41**	**0.001**
Longitude	**0.93**	**0.36**	**0.45**	**0.001**
Latitude	0.92	0.40	0.02	0.77
Slope	0.19	-0.98	0.05	0.44
Aspect	0.67	0.74	0.09	0.23
Elevation	**0.99**	**0.06**	**0.20**	**0.03**
Peat Depth	-0.09	-0.99	0.06	0.36

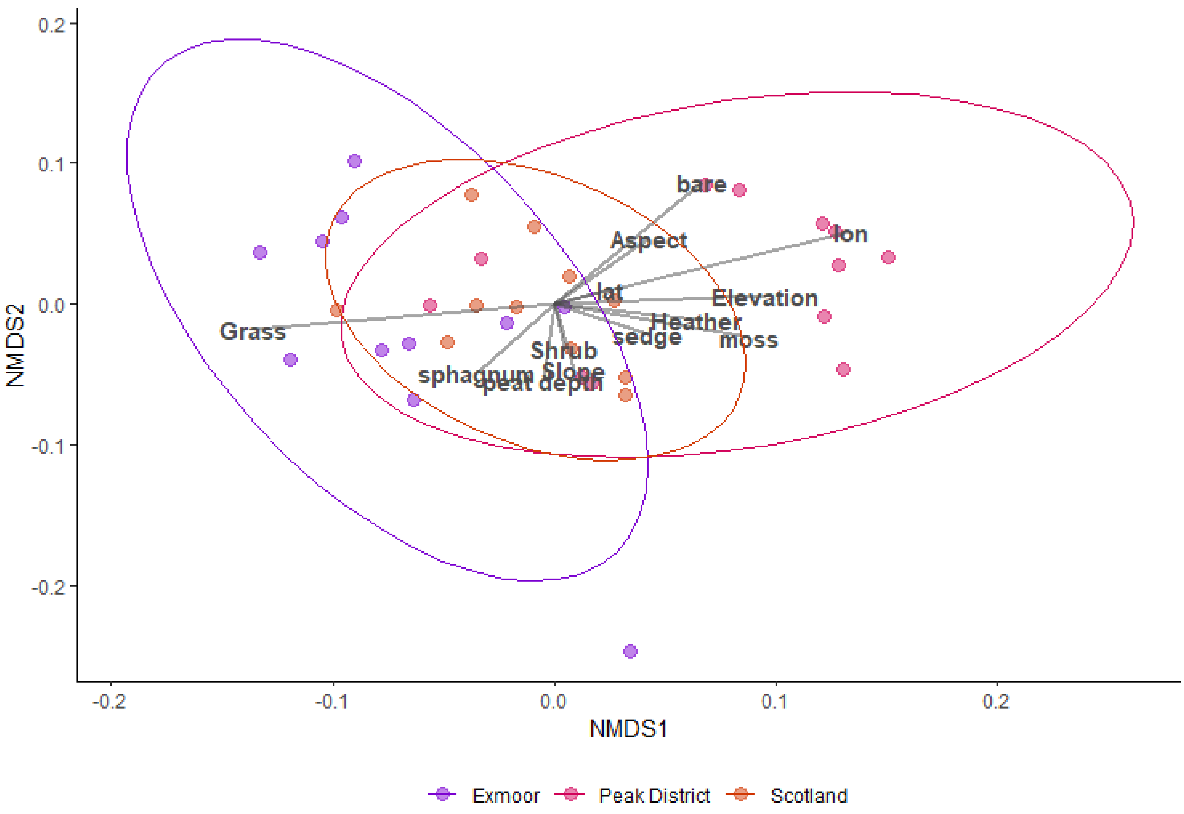


Figure 5.8 Non-metric multidimensional scaling analysis (NMDS) of vegetation groups and environmental parameters controlling soil quality parameters (bulk density, soil moisture, % C_{org}, and C:N) see Table 5.4) from three blanket bog regions (Exmoor, the Peak District, and Scotland). Ellipse show grouping of cores taken from the same region.

5.3.3 Water quality

The following results describe the water quality of soil porewaters collected from the peat mesocosms using 0.6 µm rhizon samplers between July 2019 and November 2022 as outlined in Chapter 3.

5.3.3.1 Dissolved organic carbon (DOC)

DOC concentration ranged from 4.31 mg L^{-1} to 196.15 mg L^{-1} with a median of 39.74 mg L^{-1} and a mean of 44.65 ± 27.79 mg L^{-1} (Table 5.6). DOC concentration differed significantly between restoration status (KW chi-squared = 19.19, df = 3, $p < 0.001$) whereby the median concentration was lowest in 5Y (34.06 mg L^{-1}) and highest in intact (47.99 mg L^{-1}) cores. At the site level, there were significant differences between RS (Figure 5.9 C) shown in Table 5.7. Exmoor had significantly lower concentrations compared to Scotland and the Peak District (KW chi-squared = 75.34, df = 2, $p < 0.001$, post-hoc Tukey $p < 0.01$) along with the lowest soil % C_{org} and C:N as detailed in Section 5.3.2 (Figure 5.7).

Table 5.5 Descriptive statistics for DOC concentration (mg L^{-1}) of mesocosm central vegetated core pore water from three UK blanket bog sites (Exmoor, the Peak District, and Scotland) under different restoration status' (10- and 5- year post restoration, degraded, and intact). SD refers to standard deviation.

Site	Management	Minimum	Maximum	Median	Mean	SD	No of samples
All	-	4.31	196.15	39.74	44.65	27.79	323
Scotland	All samples	5.87	152.35	25.61	54.50	25.61	108
	10Y	5.87	127.70	60.96	63.29	27.81	27
	5Y	13.67	80.03	37.59	41.39	18.00	27
	Degraded	24.77	152.35	55.99	62.97	28.49	27
	Intact	24.95	103.86	47.99	50.34	20.96	27
Peak District	All samples	15.71	123.91	45.34	47.91	21.88	108
	10Y	17.11	57.87	35.02	35.23	10.34	27
	5Y	15.83	104.22	48.00	52.88	22.75	27
	Degraded	15.71	70.38	18.30	41.05	16.90	27
	Intact	33.60	123.91	52.57	62.50	24.44	27
Exmoor	All samples	4.31	196.15	22.39	31.42	30.24	107
	10Y	6.71	193.73	20.39	63.29	36.26	26
	5Y	4.31	196.15	14.32	41.39	41.87	26
	Degraded	8.41	59.23	18.30	62.97	11.64	26
	Intact	12.61	84.40	40.17	50.34	17.58	26

Table 5.6 Results of Pairwise Wilcoxon post hoc testing for mesocosm porewater DOC concentrations for within site restoration status (10- and 5-year post restoration, degraded, and intact) differences at each of the three UK blanket bog sites. Significant differences are indicated in **bold ($p < 0.05$)**. Near significant differences are shown in *italics*.

Scotland			
	10Y	5Y	Degraded
5Y	0.56	-	
Degraded	0.81	0.06	-
Intact	0.22	0.97	0.77
Peak District			
	10Y	5Y	Degraded
5Y	0.27	-	
Degraded	**0.04**	0.84	-
Intact	**0.003**	0.96	*0.06*
Exmoor			
	10Y	5Y	Degraded
5Y	1.00	-	
Degraded	0.98	0.99	-
Intact	0.75	0.36	*0.07*

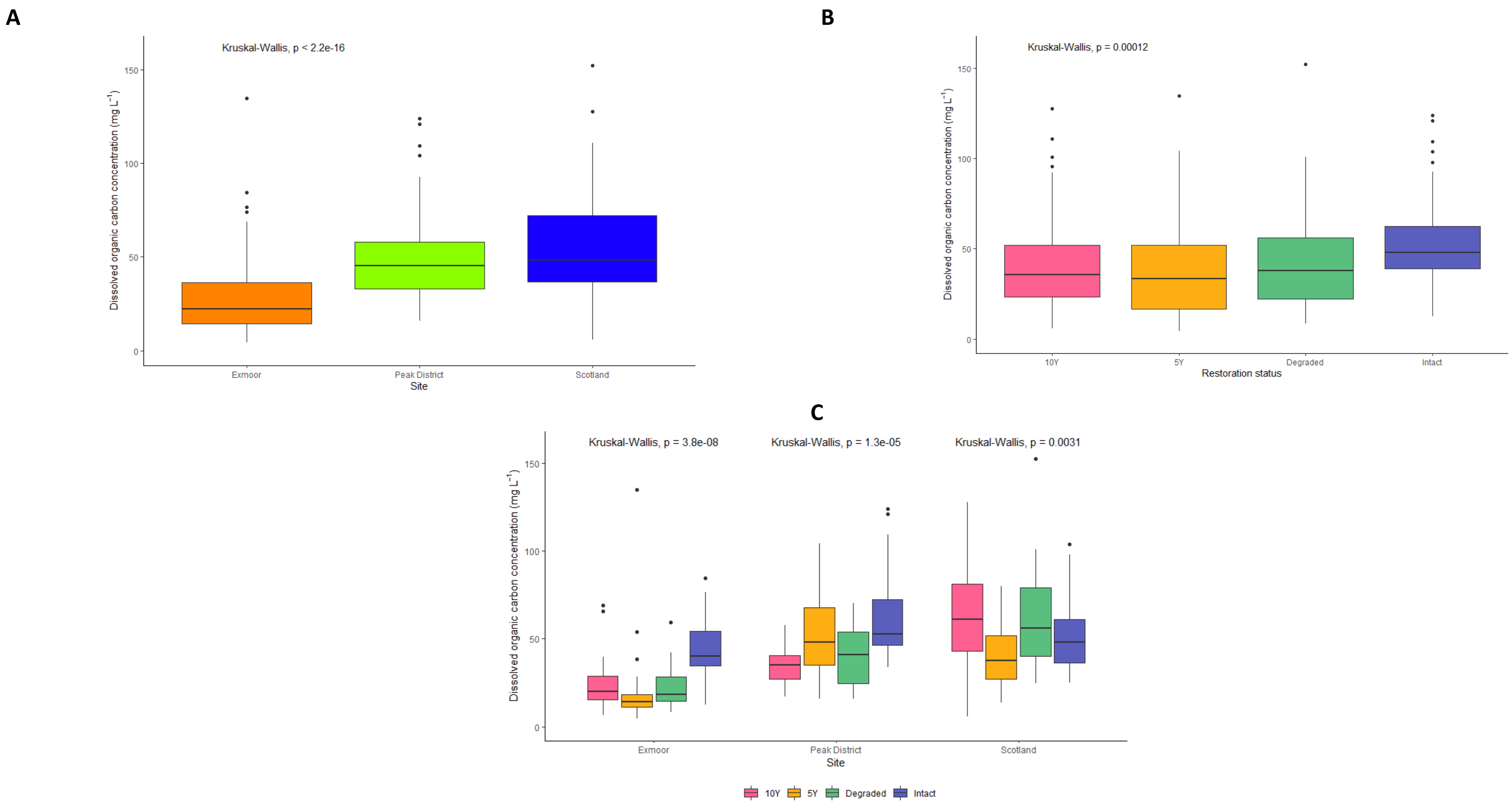


Figure 5.9 Dissolved organic carbon (DOC) concentrations of mesocosm pore waters from (**A**) three blanket bog regions in the UK (Exmoor, the Peak District, and Scotland) classified by (**B**) restoration status (10- and 5-year post restoration, degraded, and intact). **C** shows within site differences. Outliers are shown beyond the whiskers. Two outliers (DOC concentration > 180 mg L^{-1}) were removed according to statistical analysis methodology. n = 323. Kruskal Wallis significance testing results are shown.

As shown in Chapter 4, DOC and DON concentrations were significantly correlated (Spearman's correlation; $R = 0.50$, $p < 0.01$) however, DON concentration did not exhibit the same significant differences between sites as seen with DOC. DON concentration did differ significantly between restoration status (KW chi-squared = 19.62, df = 3, $p < 0.001$) however post-hoc testing indicated that this difference was only between intact and 5Y, and 10Y samples (Pairwise Wilcoxon = 0.0005 and 0.02 respectively).

DOC concentration was significantly correlated (method = Kendall) with % *C. vulgaris* ($R = 0.28$, $p < 0.01$), grass ($R = -0.48$, $p < 0.01$), and sedge ($R = 0.19$, $p < 0.01$) coverage. Cores from Exmoor had significantly higher grass coverage (KW chi-squared = 218.17, df = 2, $p < 0.01$; pair-wise Wilcoxon $p < 0.001$ with the Peak District and Scotland) and significantly lower porewater DOC whilst *C. vulgaris* was most strongly associated with Scotland and the Peak District where median DOC concentration was shown to be significantly higher (Figure 5.7 A).

DOC concentration differed significantly (Figure 5.10) between cores dominated by different vegetation groups (ANOVA, $F = 4.789$, df = 9, $p < 0.01$, post-hoc differences presented in Table 5.8), however, when site and RS are accounted for, this difference was no longer significant (ANOVA, site*vegetation group $F = 0.866$, df = 5, $p = 0.50$ and $F = 1.670$, df = 1.670, $p = 0.087$), again suggesting site and RS differences are more significant in driving DOC differences. The median DOC concentration for cores dominated by shrub was the highest of all dominant vegetation types (Figure 5.8) whilst grass was the lowest.

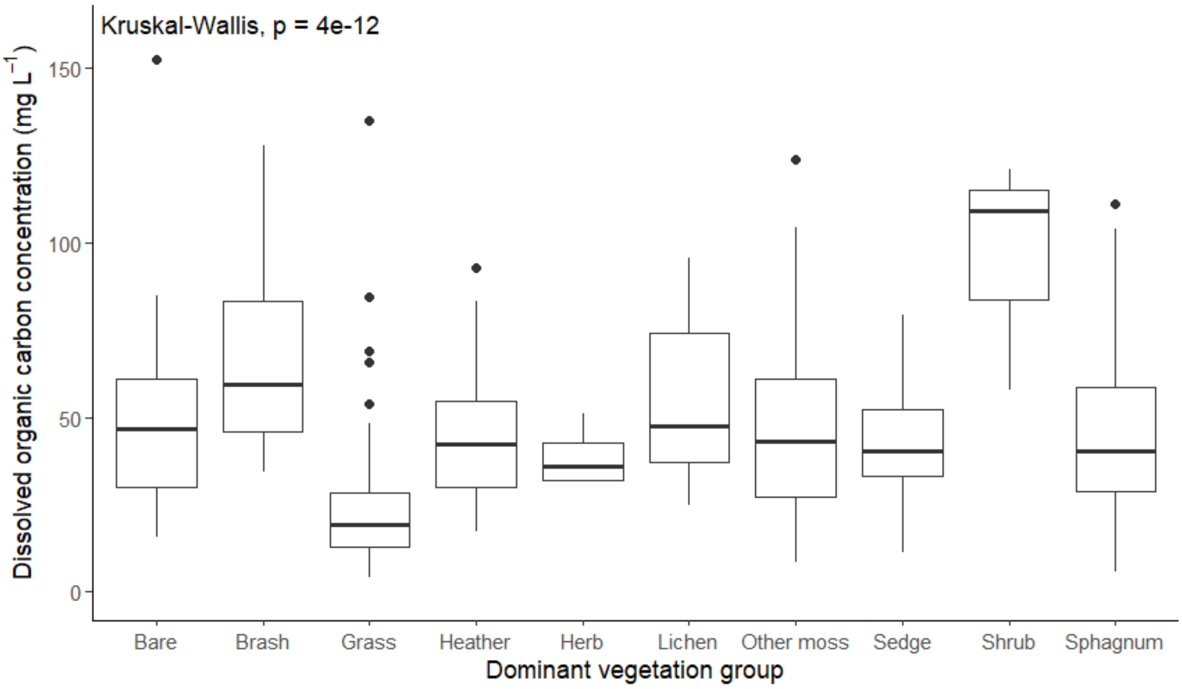


Figure 5.10 Dissolved organic carbon concentration (mg L^{-1}) of mesocosm porewater from three regions of blanket bog (Exmoor, the Peak District and Scotland) in the UK and mesocosm core dominant vegetation group. Two outliers removed (DOC concentration > 180 mg L^{-1}). Kruskal Wallis significance testing result are shown.

Table 5.7 Post-hoc (pairwise Wilcoxon test) p values for differences in dissolved organic carbon concentrations and mesocosm core dominant vegetation groups. Significant differences shown in bold. Near significant differences shown in *italics*.

	Bare	Brash	Grass	Heather	Herb	Lichen	Other moss	Sedge	Shrub
Brash	0.58	-	-	-	-	-	-	-	-
Grass	**< 0.001**	**< 0.01**	-	-	-	-	-	-	-
Heather	1.00	0.21	**< 0.01**	-	-	-	-	-	-
Herb	1.00	0.84	0.88	1.00	-	-	-	-	-
Lichen	1.00	1.00	**0.03**	1.00	1.00	-	-	-	-
Other moss	1.00	0.43	**< 0.001**	1.00	1.00	1.00	-	-	-
Sedge	1.00	**0.04**	**< 0.001**	1.00	1.00	1.00	1.00	-	-
Shrub	0.78	1.00	0.433	0.43	0.43	1.00	0.85	0.49	-
Sphagnum	1.00	*0.06*	1.00	1.00	1.00	1.00	1.00	1.00	0.57

5.3.3.1.1 Dissolved organic carbon - cut versus uncut cores

DOC concentration of porewaters in the uncut (i.e. with roots) and cut (i.e. mainly microbial) auxiliary cores were analysed with the aim of separating C fluxes. Median DOC concentration of central vegetated cores was 39.15 mg L^{-1} and was significantly lower than DOC concentration in the cut side cores (median concentration 47.18 mg L^{-1}; KW chi-squared = 9.50, df = 2, p = 0.08, post-hoc $p < 0.01$). There was no significant difference in uncut and cut side cores (post-hoc p = 0.19).

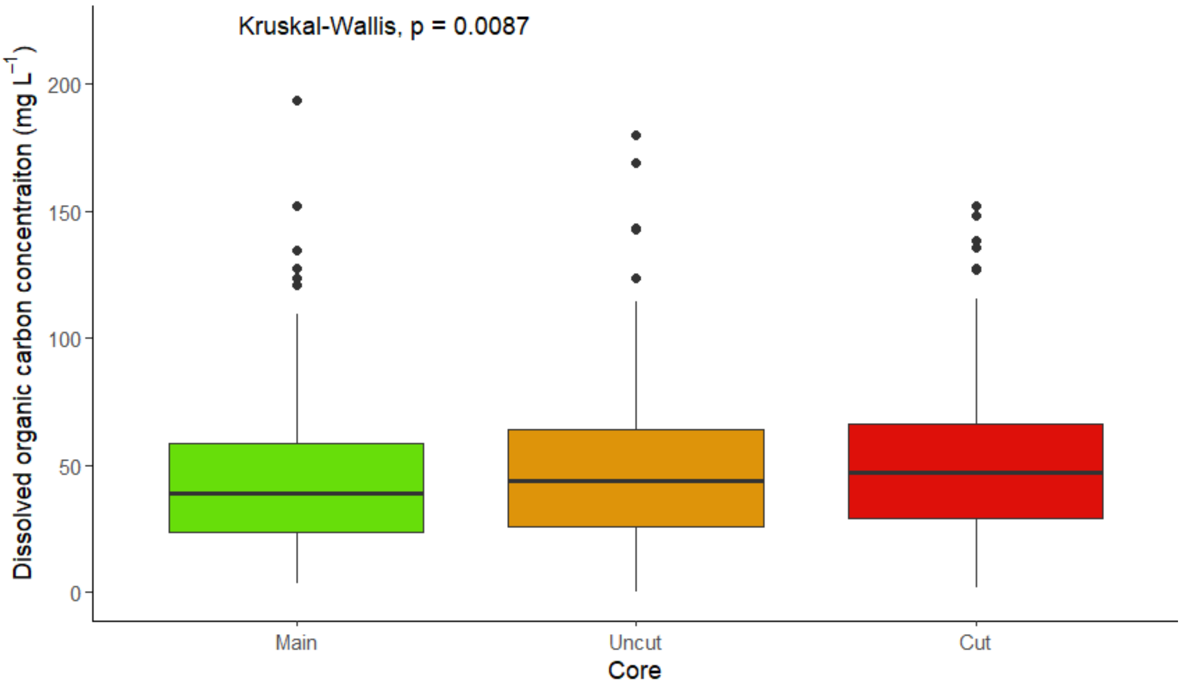


Figure 5.11 Dissolved organic carbon concentration (mg L^{-1}) of mesocosm central vegetated core (main), and two side cores which were devoid of vegetation. Uncut refers to the side core where roots were permitted to grow and cut refers to the side core where roots were cut. Kruskal-Wallis test result is displayed.

5.3.3.1.2 Drivers of dissolved organic carbon concentrations

GLM modelling (following methodology as described in Section 4.3.5.3) was undertaken to determine significant drivers of differences in DOC concentration in the central, vegetated mesocosm cores. Environmental variables (i.e., average weather conditions over the month samples were collected) and vegetation coverage were tested for correlation with DOC concentration. DON concentration, air temperature, pH, conductivity, and % coverage of grass and shrub were all significantly correlated.

Variables were then removed due to collinearity and VIF values > 4. % shrub coverage, conductivity, and pH were removed in this way. Significant variables are shown in bold in Table 5.9 along with model results. DON concentration and air temperature were significantly positively correlated with DOC concentration whilst % grass coverage was negatively correlated with DOC concentration (Figure 5.12).

Table 5.8 Estimates, error, T value, P value and VIF values of a general linear model assessing the impact of environmental variables and vegetation coverage upon DOC concentration. Significant variables are shown in **bold**.

Coefficients	Estimate	Std. Error	T value	*p*-value	VIF	AIC
Intercept	14.39	4.69	3.07	0.002		2275.81
DON concentration (mg L^{-1})	**9.17**	**1.05**	**8.73**	**< 0.001**	**1.01**	
Air temperature (°C)	**1.77**	**0.33**	**5.28**	**< 0.001**	**1.00**	
% grass coverage	**-0.31**	**0.06**	**-4.91**	**< 0.001**	**1.01**	

As shown in Figure 5.10, DOC concentration was highest in cores dominated by shrub, and it was therefore hypothesised prior to undertaking GLM analysis, that shrub would be a significant driver. Shrub was absent from Exmoor cores whilst grass (which was identified as being a significant driver of differences in DOC concentration) dominated Exmoor cores. Therefore, to determine drivers in DOC in more typical UK blanket bog, data from Exmoor samples were removed from the data set (109 samples) and the analysis re-ran. Air temperature, % shrub and brash coverage were found to be significantly correlated with DOC concentration (Table 5.10).

Table 5.9 Estimates, error, T value, P value and VIF values of a general linear model assessing the impact of environmental variables and vegetation coverage upon DOC concentration for samples from Scotland and the Peak District mesocosm cores. Significant variables are shown in **bold**.

Coefficients	Estimate	Std. Error	T value	*p*-value	VIF	AIC
Intercept	58.86	22.51	2.62	0.009		1534.5
Air temperature	**1.65**	**0.44**	**3.80**	**0.0002**	**1.10**	
% shrub coverage	**0.56**	**0.18**	**3.02**	**0.003**	**1.00**	
% brash coverage	**0.40**	**0.11**	**3.54**	**0.0005**	**1.03**	
pH	-7.87	4.78	-1.65	0.10	1.13	

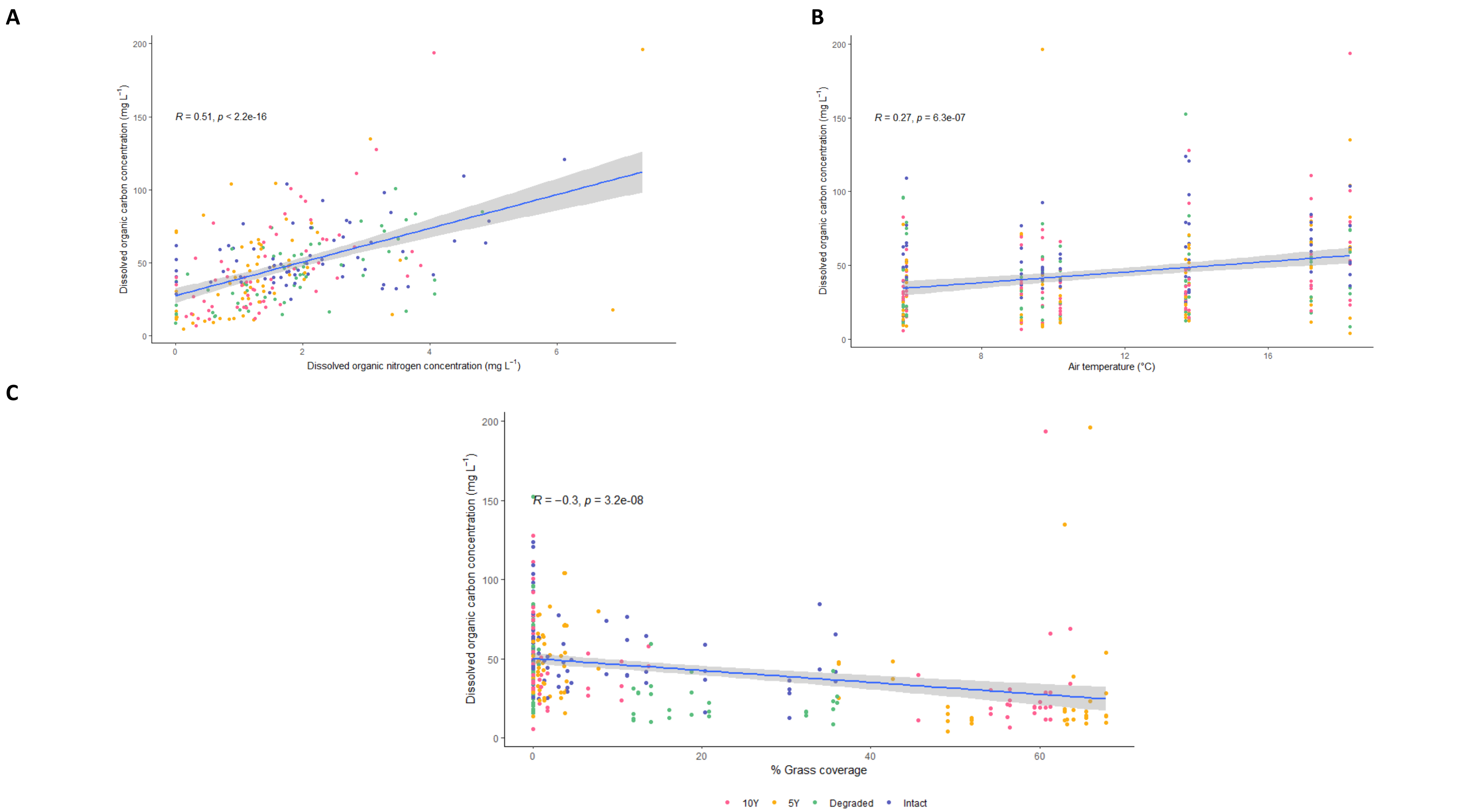


Figure 5.12 Linear correlation between dissolved organic carbon correlation (DOC mg L^{-1}) and significant variables identified with generalised linear modelling (A = dissolved organic nitrogen, B = Air temperature, and C = % grass coverage). Line of best fit plotted. Shaded area shows the 95 % confidence level. R and significance values shown (method = Pearson). Colours indicate the four-restoration status' (10- and 5- year post restoration, degraded, and intact).

5.3.3.2 UV absorbance

As with cores from grouse-managed blanket bog, all mesocosm porewaters from the regional blanket bog were scanned for specific wavelengths (UV_{254}, UV_{400}, UV_{465} and UV_{665}) and the majority (dependent upon Covid-19 restrictions) of central vegetated mesocosm cores were scanned for broad spectrum (230-800 nm) UV absorbance.

5.3.3.2.1 UV_{254} and $SUVA_{254}$

UV_{254} ranged from 0.056 cm^{-1} to 5.41 cm^{-1} with a median of 1.89 ± 1.30 cm^{-1} and a mean of 2.03 ± 1.24 (Table 5.11). Intact samples had the highest median absorbance of 2.16 cm^{-1} and 5Y had the lowest median absorbance of 1.52 cm^{-1}. UV_{254} absorbance differed significantly between RS (KW chi-squared = 22.25, df = 3, $p < 0.001$) and post-hoc testing indicated that intact samples had a significantly higher absorbance compared to 5Y and 10Y samples. When DOC concentration is accounted for (i.e., $SUVA_{254}$), there was a significant difference between RS (KW chi-squared = 8.28, df = 3, $p = 0.04$) but post-hoc testing indicated no significant differences between groups. At the site level, UV_{254} differed significantly between RS at all sites however for $SUVA_{254}$, this difference was only significant between RS in cores from Scotland (intact cores had a significantly higher $SUVA_{254}$ compared to the other RSs and degraded cores had a significantly higher $SUVA_{254}$ compared to the post-restoration cores; Figure 5.13). UV_{254} absorbance differed significantly with dominant vegetation group (KW chi-squared = 81.09, df = 2, $p < 0.01$; post-hoc differences presented in Table 5.12).

$SUVA_{254}$ differed significantly between dominant vegetation group (KW chi-squared = 38.22, df = 2, $p < 0.01$; Figure 5.14) with cores dominated by grass having the lowest median $SUVA_{254}$ (0.64 L mg^{-1} m^{-1}) and brash cores had the highest (2.73 L mg^{-1} m^{-1}). Significant differences between dominant vegetation groups are presented in Table 5.13.

Table 5.10 Descriptive statistics for $SUVA_{254}$ of mesocosm central vegetated core pore water from regional blanket bog sites in the UK (Exmoor, the Peak District, and Scotland) classified by restoration status (10- and 5-years post restoration, degraded, and intact). SD refers to standard deviation.

Site	Management	Minimum	Maximum	Median	Mean	SD	No of samples
All	-	0.32	37.99	4.52	5.09	3.57	322
Scotland	All samples	0.45	37.99	2.26	5.17	2.26	108
	10Y	1.87	37.99	2.68	5.68	6.61	27
	5Y	0.45	8.08	1.42	3.86	1.58	27
	Degraded	1.99	13.42	2.98	5.36	2.68	27
	Intact	3.7	11.57	2.53	5.76	1.93	27
Peak District	All samples	1.56	20.75	2.19	5.60	2.19	108
	10Y	2.58	15.60	1.41	4.98	2.64	27
	5Y	1.56	18.33	2.31	5.61	3.20	27
	Degraded	2.29	20.75	2.25	6.83	3.83	27
	Intact	2.11	10.80	2.86	5.15	2.62	27
Exmoor	All samples	0.45	22.99	2.26	4.50	3.67	106
	10Y	0.89	8.86	0.58	3.66	2.24	26
	5Y	0.44	22.99	0.63	4.70	4.56	27
	Degraded	1.09	17.11	0.75	5.02	4.26	26
	Intact	0.32	14.79	1.86	4.63	3.22	27

Table 5.11 Post-hoc (pairwise Wilcoxon test) p values for differences in UV_{254} absorbance and mesocosm core dominant vegetation groups. Significant differences shown in bold.

	Bare	Brash	Grass	Heather	Herb	Lichen	Other moss	Sedge	Shrub
Brash	1.00	-	-	-	-	-	-	-	-
Grass	**< 0.0001**	**< 0.001**	-	-	-	-	-	-	-
Heather	**0.002**	**0.01**	**0.0002**	-	-	-	-	-	-
Herb	1.00	1.00	0.91	1.00	-	-	-	-	-
Lichen	1.00	1.00	**0.18**	1.00	1.00	-	-	-	-
Other moss	1.00	1.00	**< 0.001**	1.00	1.00	1.00	-	-	-
Sedge	**0.03**	**0.22**	**0.0002**	1.00	1.00	1.00	1.00	-	-
Shrub	1.00	1.00	0.94	1.00	1.00	1.00	1.00	1.00	-
Sphagnum	0.34	*0.94*	< 0.001	1.00	1.00	1.00	1.00	1.00	1.00

Table 5.12 Post-hoc (pairwise Wilcoxon test) p values for differences in $SUVA_{254}$ absorbance and mesocosm core dominant vegetation groups. Significant differences shown in **bold**. Near significant differences shown in *italics*.

	Bare	Brash	Grass	Heather	Herb	Lichen	Other moss	Sedge	Shrub
Brash	0.67	-	-	-	-	-	-	-	-
Grass	**0.00049**	1.00	-	-	-	-	-	-	-
Heather	**0.0001**	1.00	1.00	-	-	-	-	-	-
Herb	1.00	1.00	1.00	1.00	-	-	-	-	-
Lichen	1.00	1.00	1.00	1.00	1.00	-	-	-	-
Other moss	1.00	1.00	0.05	0.20	1.00	1.00	-	-	-
Sedge	0.38	1.00	1.00	1.00	1.00	1.00	1.00	-	-
Shrub	*0.06*	1.00	1.00	0.99	1.00	1.00	0.89	1.00	-
Sphagnum	0.98	1.00	**0.02**	0.18	1.00	1.00	1.00	1.00	0.68

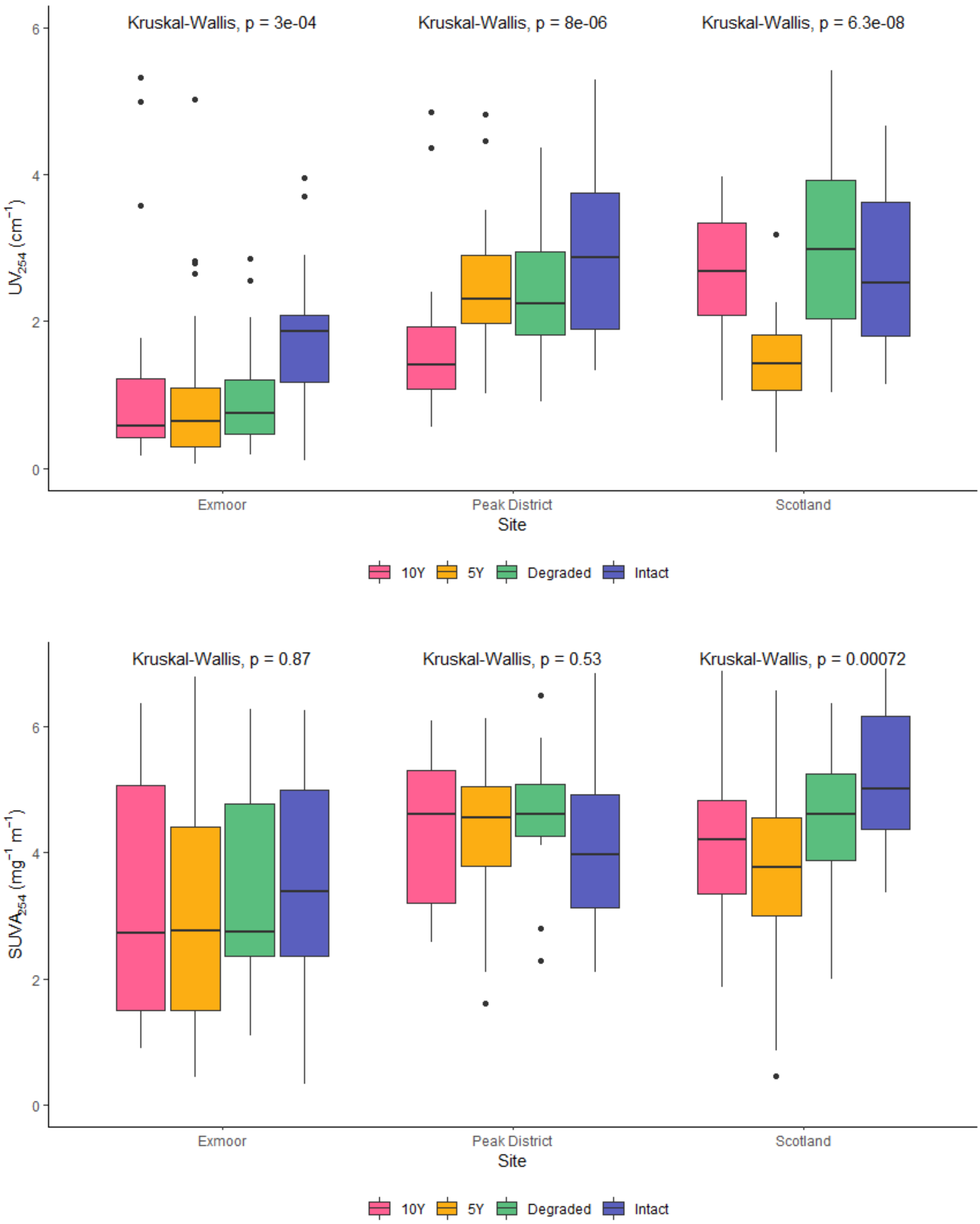


Figure 5.13 UV_{254} absorbance (cm^{-1}) and $SUVA_{254}$ (L mg^{-1} m^{-1}) of mesocosm porewaters from three blanket bog regions (Exmoor, the Peak District, and Scotland) in the UK under four restoration status' (10- and 5-years post restoration, degraded, and intact). Significance testing results shown; significance level < 0.05.

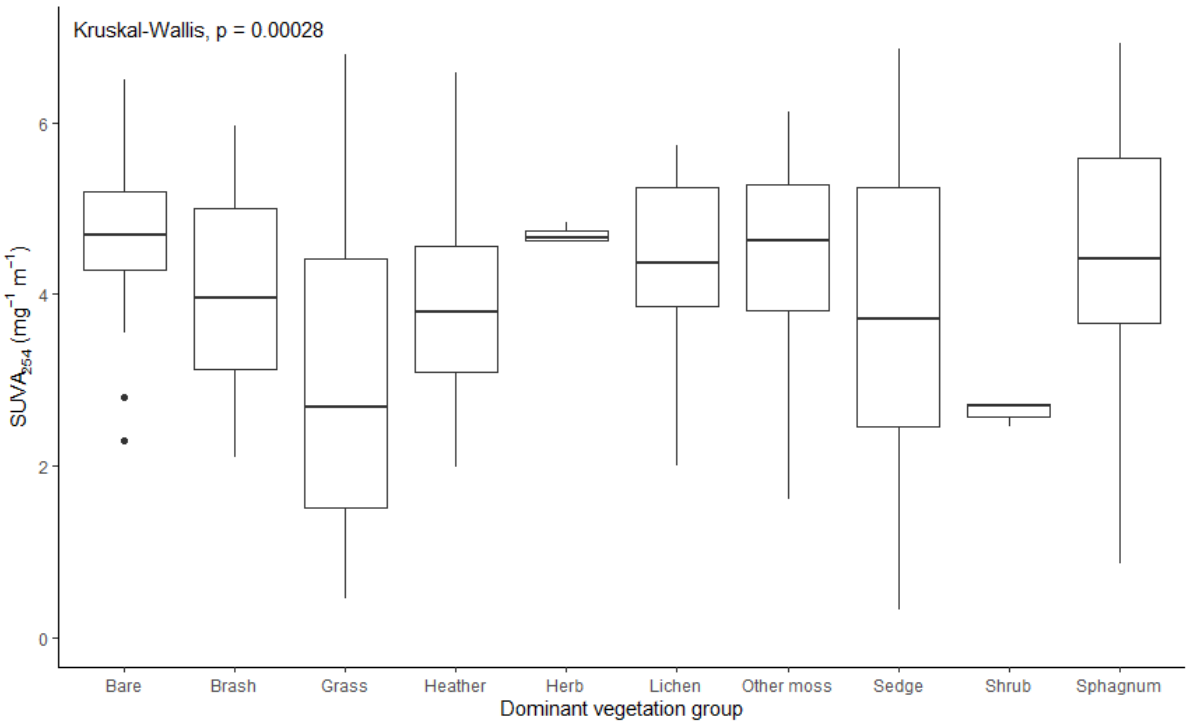


Figure 5.14 $SUVA_{254}$ (L mg^{-1} m^{-1}) of mesocosm porewaters from peat soil from three regions of blanket bog in the UK (Exmoor, the Peak District, and Scotland) under four restoration status' (10- and 5-years post restoration, degraded, and intact). Significance testing result displayed.

GLM modelling (following methodology as described in Section 5.3.3.1.2) was undertaken to determine significant drivers of differences in UV_{254}. Environmental variables (i.e., average weather conditions over the month samples were collected) and vegetation coverage were tested for correlation with UV_{254}. DOC and DON concentration, air temperature, light level, year of collection, pH, conductivity, and % coverage of grass, brash, and bare ground were all significantly correlated. Variables were then removed due to collinearity and VIF values > 4. Soil moisture, air temperature, light level and brash were removed in this way. Significant variables are shown in bold in Table 5.14 along with model results. DOC concentration and % bare ground coverage were positively correlated with UV_{254} whilst collection year and % grass coverage were negatively correlated (Figure 5.15).

Table 5.13 Estimates, error, T value, P value and VIF values of a general linear model assessing the impact of environmental variables and vegetation coverage upon UV_{254} absorbance. Significant variables are shown in **bold**.

Coefficients	Estimate	Std. Error	T value	*p*-value	VIF	AIC
Intercept	611.67	124.16	4.93	< 0.0001		825.53
Collection year	**-3.02**	**0.061**	**-4.92**	**< 0.0001**	**1.004**	
DOC concentration (mg L^{-1})	**0.024**	**0.002**	**13.35**	**< 0.0001**	**1.114**	
% grass coverage	**-0.13**	**0.002**	**-5.65**	**< 0.0001**	**1.156**	
% bare ground coverage	**0.005**	**0.002**	**3.04**	**0.0026**	**1.051**	

As with GLM modelling for DOC concentration, analysis was repeated for UV254 absorbance excluding Exmoor samples from the data set. DOC concentration, air temperature, pH, % *C. vulgaris*, shrub, and grass coverage were included in the original model. pH was removed due to a high VIF value. Variables included in the final model are shown in Table 5.15. As with the GLM excluding Exmoor data for DOC concentration, shrub was found to be a significant driver of UV_{254} absorbance.

Table 5.14 Estimates, error, T value, P value and VIF values of a general linear model assessing the impact of environmental variables and vegetation coverage upon DOC concentration for samples from Scotland and the Peak District mesocosm cores. Significant variables are shown in **bold**.

Coefficients	Estimate	Std. Error	T value	*p*-value	VIF	AIC
Intercept	1.68	0.20	8.25	< 0.0001		564.8
Air temperature	-0.008	0.115	-0.6	0.55	1.14	
DOC concentration	**0.02**	**0.003**	**8.93**	**< 0.001**	**1.21**	
% C. vulgaris	**-0.02**	**0.005**	**-4.46**	**< 0.001**	**1.09**	
% shrub	**-0.02**	**0.006**	**-2.96**	**0.003**	**1.06**	
% grass	-0.02	0.01	-1.52	0.13	1.09	

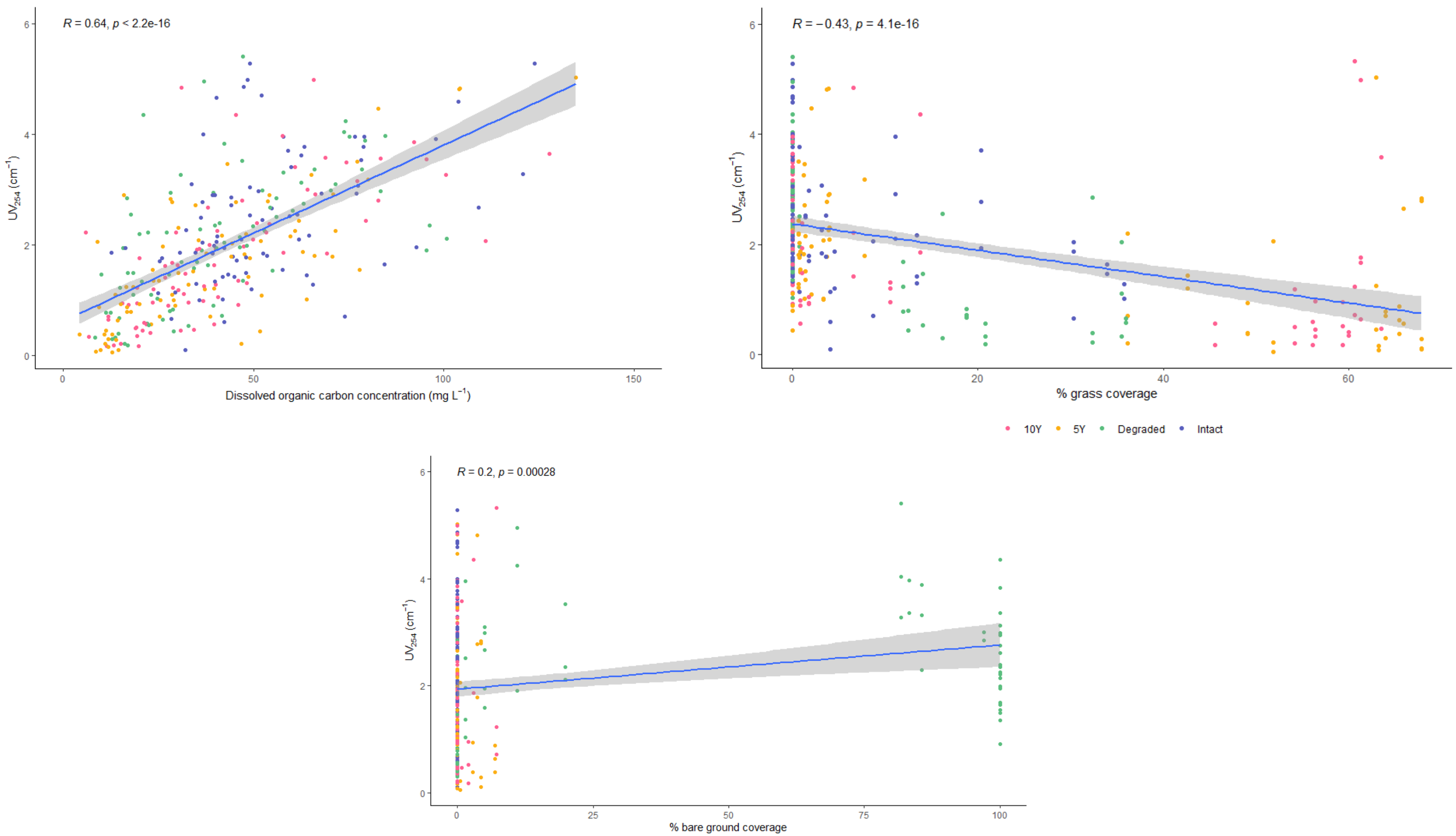


Figure 5.15 Linear correlation between UV_{254} absorbance and significant variables identified with generalised linear modelling. Collection year excluded from graphic due to being assigned as a factor. Line of best fit plotted. Shaded area shows the 95 % confidence level. R and significance values shown (method = Pearson). Colours indicate the four-restoration status' (10- and 5- year post restoration, degraded, and intact).

5.3.3.2.2 Hazen

Hazen ranged from 3.6 to 1438 with a median of 297 and a mean of 360 ± 284. There was a significant difference in hazen values of porewaters from cores from different RSs (KW chi-squared = 23.147, df = 3, $p < 0.01$) with intact cores having significantly higher hazen compared to 10Y and 5Y cores (median hazen 355, 211, and 355 respectively; Figure 5.16). Samples from Exmoor had significantly lower hazen compared to porewaters from cores from the Peak District and Scotland (KW chi-squared = 80.62, df = 2, $p < 0.01$; post-hoc $p < 0.001$). Hazen significantly correlated with DOC concentration ($R = 0.54$, $p < 0.01$, method = Pearson) and as with UV_{254}, there was a significant negative correlation with % grass coverage ($R = -0.43$, $p < 0.01$).

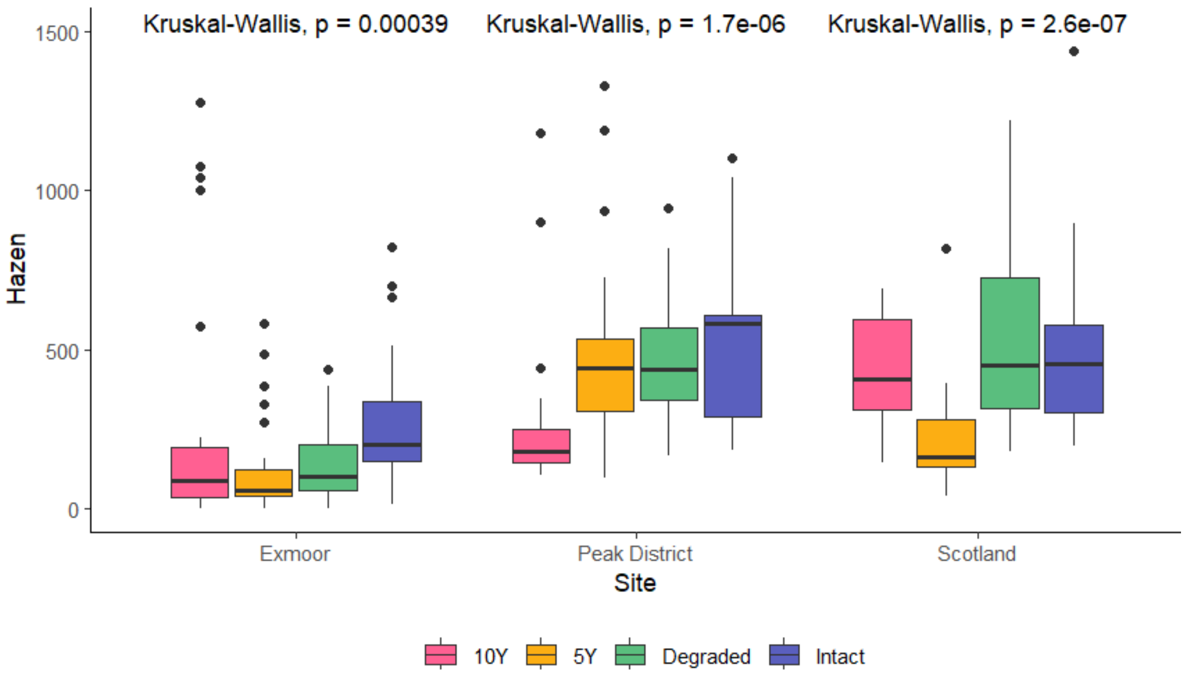


Figure 5.16 Hazen of mesocosm porewaters from three regions of blanket bog in the UK (Exmoor, the Peak District, and Scotland) classified under 4 restoration status' (10- and 5-year post restoration, degraded, and intact). Significance testing results for within site differences shown. Outliers shown beyond the whiskers. Two outlier results removed (hazen > 1500).

5.3.3.2.3 E4:E6

E4:E6 (ratio of absorbance at UV_{465} and UV_{665}) ranged from 0.02 to 22.5 with a median of 4.21 and mean of 4.90 ± 3.65 (12 outlier results removed; ratio > 30). E4:E6 differed significantly between RS (KW chi-squared = 10.10, df = 3, p = 0.01) with degraded cores having the highest mean of 5.63 ± 3.89 compared to 10Y cores which had the lowest mean of 4.29 ± 3.24. Samples from Exmoor cores had significantly lower E4:E6 (mean 3.18 ± 3.24) compared to both the Peak District (6.21 ± 3.78) and Scotland (5.28 ± 3.25). Samples from degraded cores from both the Peak District and Scotland had a higher mean E4:E6 compared to intact cores (Figure 5.17).

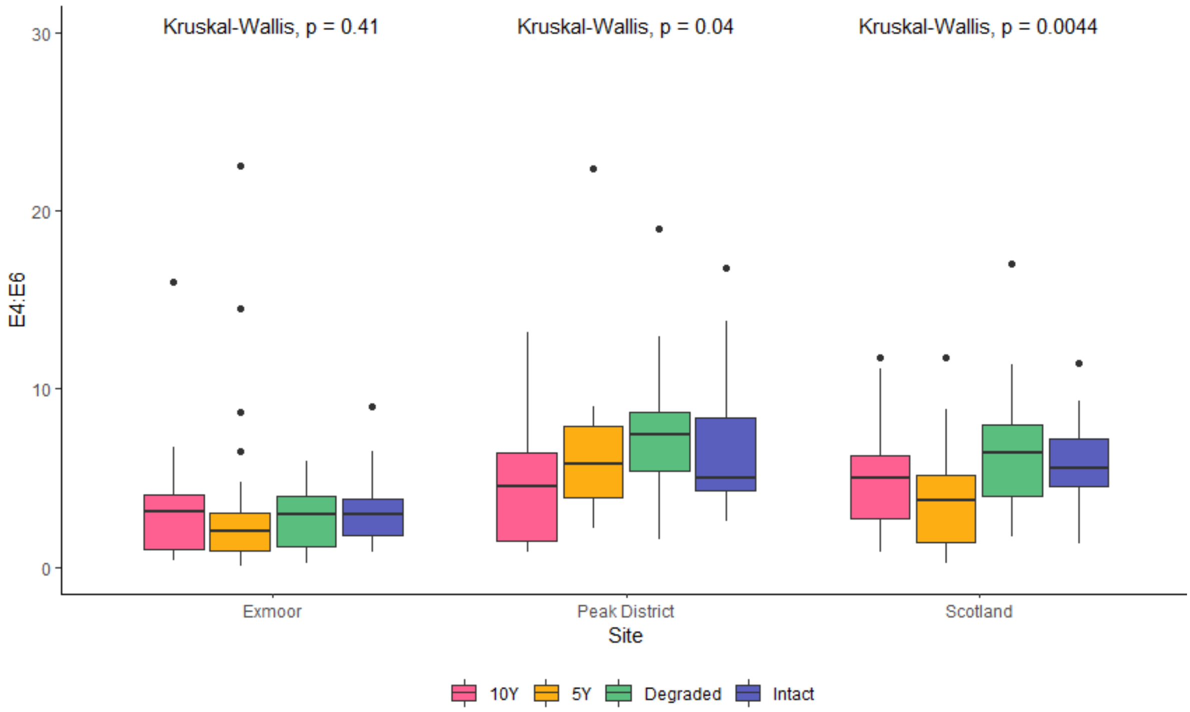


Figure 5.17 E4:E6 (Ratio of UV_{465} and UV_{665} absorbance) in mesocosm porewater samples from three regions of blanket bog in the UK (Exmoor, the Peak District, and Scotland) classified by restoration status (10- and 5-year post restoration, degraded, and intact). Significance testing results shown. 12 outliers removed (E4:E6 > 30).

5.3.3.3 pH

Mesocosm porewater pH ranged from 3.44 to 5.49 with a median of 4.35 and a mean of 4.67 ± 0.38. pH of porewaters from the Peak District were significantly lower compared to Exmoor and Scotland (means of 4.10 ± 0.31, 4.45 ± 0.34, and 4.55 ± 0.33 respectively). Within site differences were only significant in the Peak District where degraded and intact samples had significantly lower pH compared to 10Y and 5Y post-restoration samples (Figure 5.18). pH differed between samples from cores with different dominant vegetation groups (KW chi-squared = 43.50, df = 9, $p < 0.01$) with cores dominated by *Sphagnum* showing the highest mean pH (Figure 5.19). pH was significantly negatively correlated with UV_{254} ($R = -0.21$, $p < 0.001$). pH showed significant variation seasonally (KW chi-squared = 32.31, df = 2, $p < 0.01$) with a significantly lower mean pH in summer (4.30 ± 0.37) compared to winter (4.58 ± 0.38).

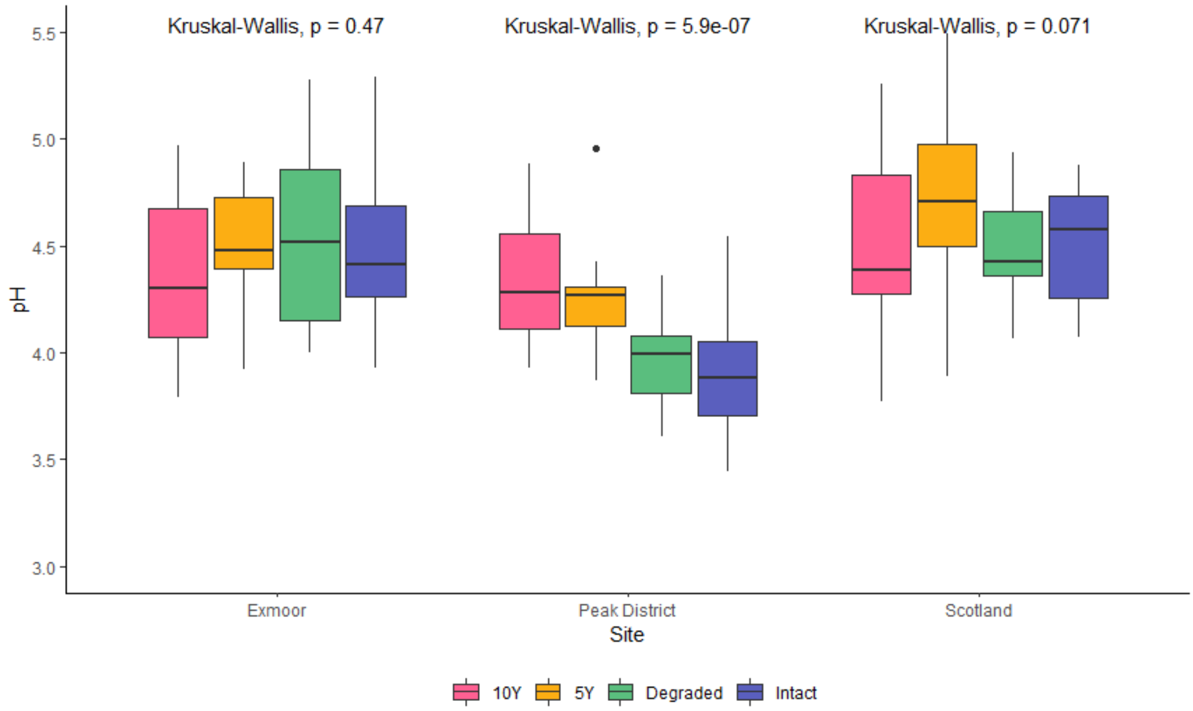


Figure 5.18 pH of mesocosm porewaters from peat cores taken from three blanket bog regions in the UK (Exmoor, the Peak District, and Scotland) classified by restoration status (10- and 5- year post restoration, degraded and intact). Significance test results for within site differences shown. Outliers shown beyond the whiskers.

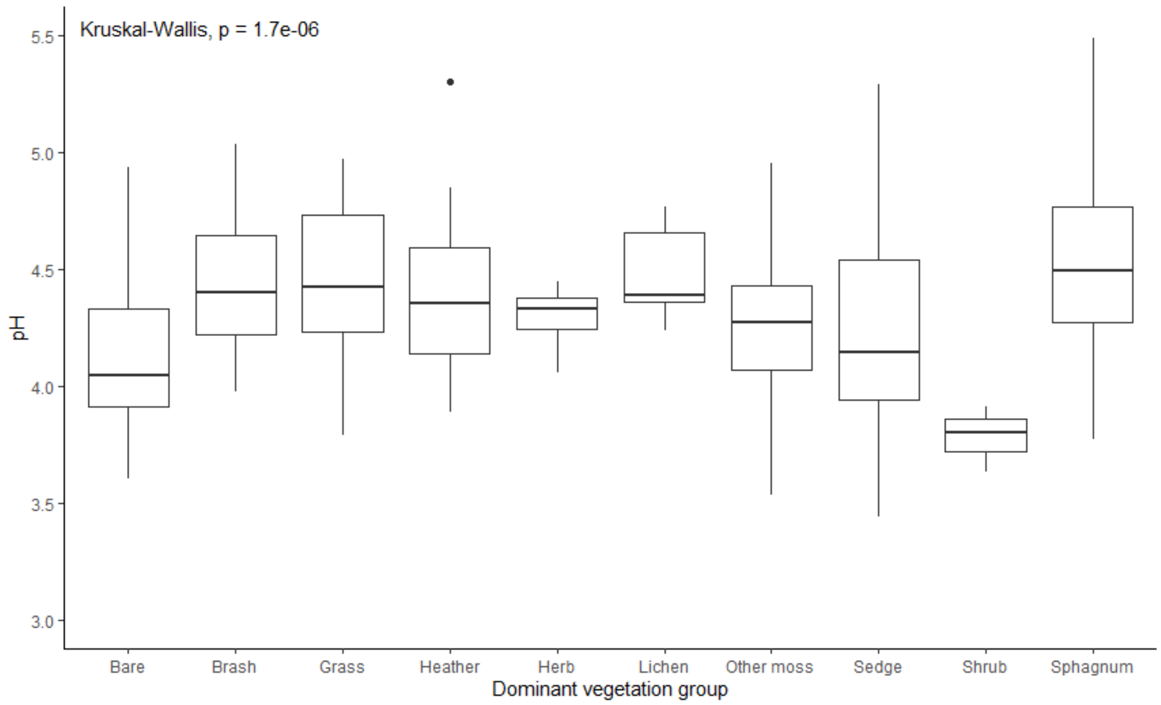


Figure 5.19 pH of mesocosm cores classified by dominant vegetation group from three regions of blanket bog in the UK (Exmoor, the Peak District, and Scotland) under four restoration status' (10- and 5-year post restoration, degraded, and intact).

5.3.3.4 Conductivity

Mesocosm porewater conductivity ranged from 11.27 µS cm^{-1} to 363.77 µS cm^{-1} with a median of 68.24 µS cm^{-1} and a mean of 77.66 ± 44.10 µS cm^{-1}. Conductivity of porewaters from Exmoor were significantly lower compared to those from the Peak District and Scotland (KW chi-squared = 10.438, df = 2, p = 0.005; means of 65.39 ± 33.44 µS cm^{-1}, 87.28 ± 55.50 µS cm^{-1}, and 80.01 ± 37.62 µS cm^{-1} respectively; Figure 5.20). Conductivity differed significantly between RS (KW chi-squared = 8.82, df = 3, p = 0.03) however post-hoc testing indicated this significant difference was only between samples from 5Y and intact cores (p = 0.026). Conductivity was significantly positively correlated with DOC concentration (R = 0.30, p < 0.001) along with DON concentration (R = 0.25, p < 0.01) and UV_{254} (R = 0.26, p < 0.01), but not with $SUVA_{254}$.

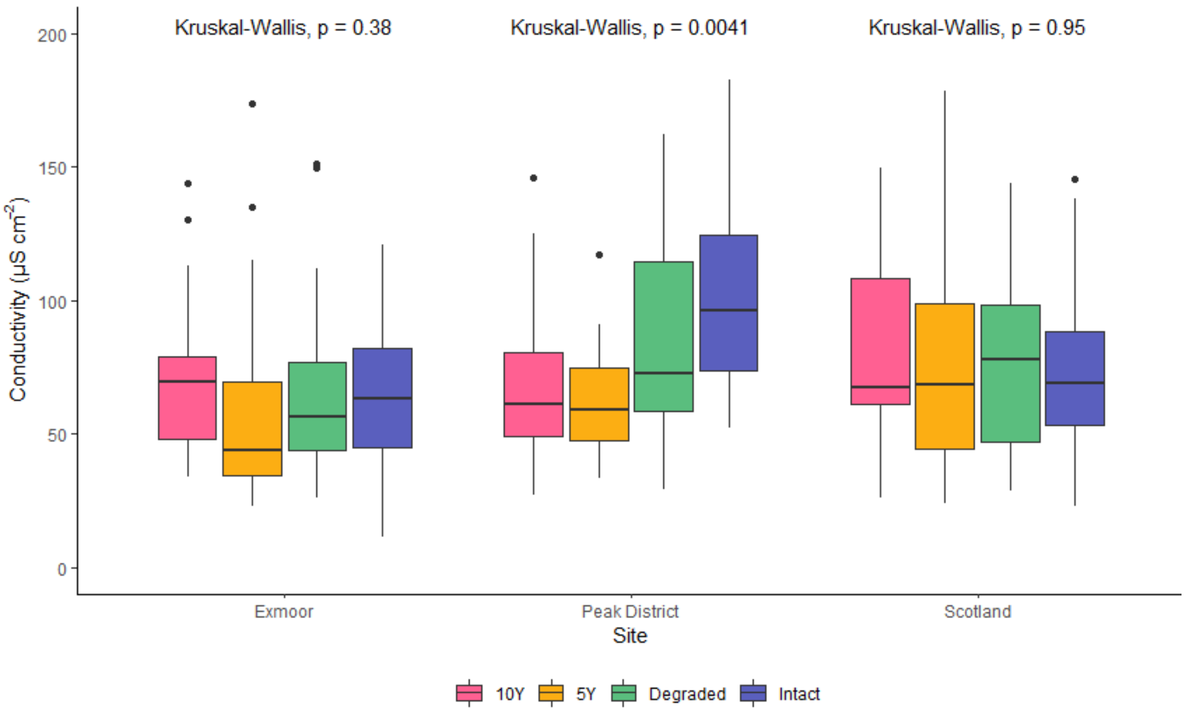


Figure 5.20 Conductivity (µS cm^{-1}) of mesocosm porewaters from three regions of blanket bog in the UK (Exmoor, the Peak District, and Scotland) classified by restoration status (10- and 5-year post restoration, degraded, and intact). Significance testing for within site differences shown. Conductivity > 200 µS cm^{-1} removed from figure ($n = 5$) according to statistical analysis methodology.

5.3.4 Gas Fluxes

5.3.4.1 Soil respiration (SR)

SR of uncut side cores (SR_{uncut}; i.e., root + microbial respiration) ranged from 0.0001 to 15.1 µmol CO_2 m^{-2} s^{-1} with a median of 0.74 µmol CO_2 m^{-2} s^{-1} whilst cut side cores (SR_{cut}; i.e., mainly microbial respiration) ranged from 0.0001 to 16.01 µmol CO_2 m^{-2} s^{-1} with a median of 0.61 µmol CO_2 m^{-2} s^{-1}. SR_{uncut} differed significantly between RS (KW chi-squared = 12.23, df = 3, $p < 0.01$) but post-hoc testing only showed significant differences between degraded cores and 5Y cores ($p < 0.05$). SR_{uncut} also differed significantly between sites (KW chi-squared = 6.31, df = 2, $p = 0.04$) however post-hoc testing indicated this significant difference was only between Scotland and Exmoor cores ($p < 0.05$). At the site level, significance differences were found between RS in cores from the Peak District and Scotland (Figure 5.21). In cores from the Peak District, degraded cores had a significantly lower SR_{uncut} compared to the other RS, and in cores from Scotland, 5Y cores had a significantly higher SR_{uncut} compared to degraded and intact cores (post-hoc $p < 0.05$). Root respiration (i.e., the difference between uncut and cut side cores) ranged from -13.83 µmol CO_2 m^{-2} s^{-1} to 9.63 µmol CO_2 m^{-2} s^{-1} with a median of 0.13 µmol

CO_2 m^{-2} s^{-1} with a negative flux representing higher SR in the cut side core compared with the uncut side core. As negative root fluxes were an artefact of decomposing cut roots, the cut cores were not considered in the subsequent analysis.

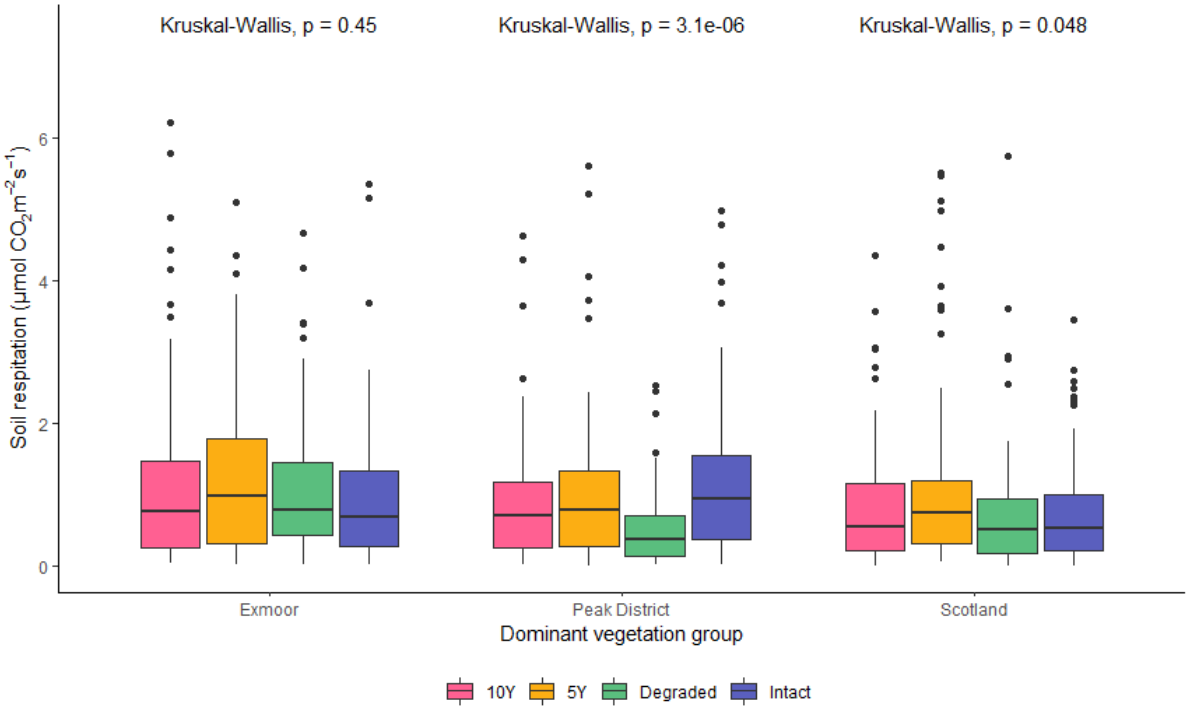


Figure 5.21 Total soil respiration carbon flux (µmol CO_2 m^{-2} s^{-1}) of uncut (i.e., roots permitted) mesocosm side cores from three regions of blanket bog in the UK (Exmoor, the Peak District, and Scotland) classified by restoration status (10- and 5-year post restoration, degraded, and intact). Significance testing based on Kruskal-Wallis for within site differences are shown.

SR_{uncut} differed significant between dominant vegetation group (KW chi-squared = 48.824, df = 10, $p < 0.01$; Figure 5.22; post-hoc significant differences between groups shown in Table 5.16). Mean SR_{uncut} was highest in cores dominated by grass (17.64 µmol CO_2 m^{-2} s^{-1}) and lowest in cores dominated by bare peat (0.37 µmol CO_2 m^{-2} s^{-1}). SR_{uncut} of cores dominated by bare peat had a significantly lower flux compared to all other vegetation groups excluding herb, lichen, and brash (Table 5.16, post-hoc $p < 0.05$).

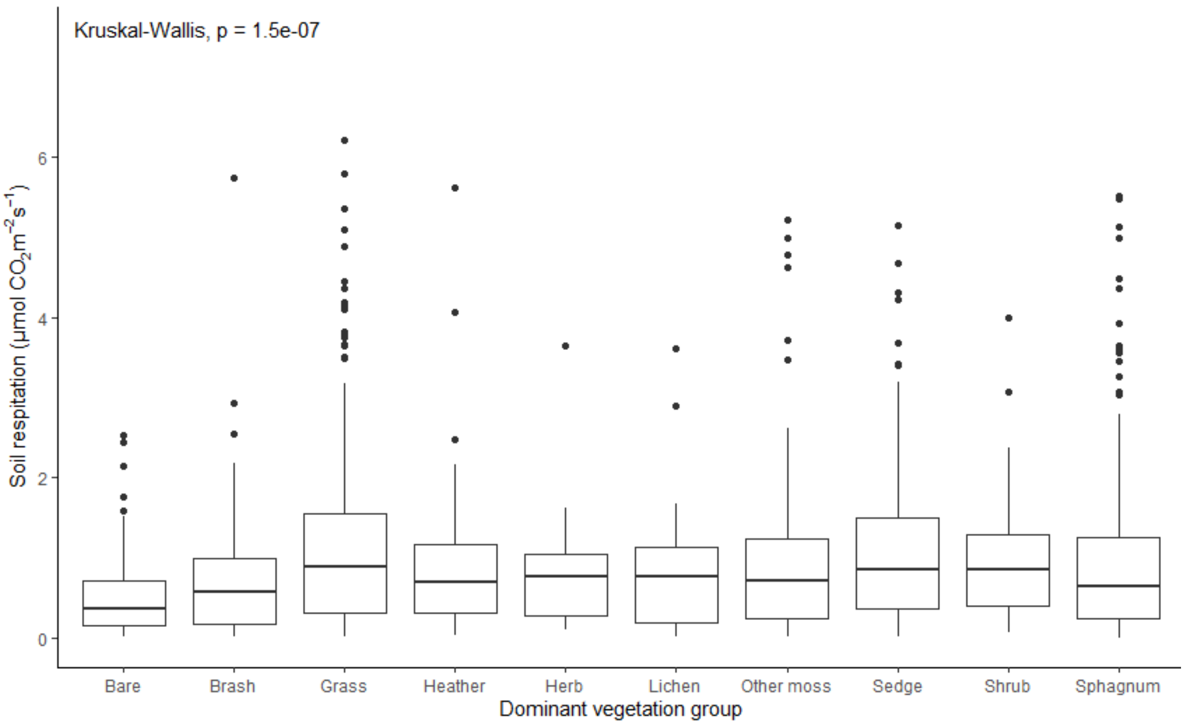


Figure 5.22 Total soil respiration (µmol CO_2 m^{-2} s^{-1}) fluxes of uncut (i.e., roots permitted) mesocosm side cores from three regions of UK blanket bog (Exmoor, the Peak District, and Scotland) classified by dominant vegetation group. Significant testing result shown. Outlier results are indicated beyond the whiskers.

Table 5.15 Post-hoc (pairwise Wilcoxon test) p values for differences in soil respiration for uncut (i.e., roots permitted) mesocosm side cores and mesocosm core dominant vegetation groups. Significant differences shown in **bold**.

	Bare	Brash	Grass
Brash	1.00	-	-
Grass	**< 0.001**	0.0187	-
Heather	**0.0083**	1.00	1.00
Herb	1.00	1.00	1.00
Lichen	1.00	1.00	1.00
Other moss	**0.0258**	1.00	1.00
Sedge	**< 0.001**	0.126	1.00
Shrub	**0.0028**	0.543	1.00
Sphagnum	**0.0028**	1.00	0.9086

5.3.4.2 Net ecosystem exchange (NEE)

NEE was measured on central vegetated mesocosm cores. NEE ranged from -32.19 µmol CO_2 m^{-2} s^{-1} to -0.01 µmol CO_2 m^{-2} s^{-1} with a median of -2.89 µmol CO_2 m^{-2} s^{-1} (Table 5.17). NEE was significantly higher (i.e. less negative) in degraded cores (KW chi-squared = 32.904, df = 3, $p < 0.01$; post-hoc $p < 0.01$). Median flux was significantly higher in degraded cores in cores from Scotland and the Peak District compared to the other restoration statuses but had the lowest flux of all Exmoor cores, but this was not significant (Figure 5.23). NEE was significantly correlated with temperature (R = -0.47, $p < 0.01$) and seasonally, differed significantly between restoration status with degraded cores having the largest NEE in each season (Figure 5.24). At the site level, degraded cores had significantly higher NEE compared to the other restoration statuses (post-hoc $p = 0.05$).

Table 5.16 Descriptive statistics for full light net ecosystem exchange (µmol CO_2 m^{-2} s^{-1}) of mesocosm cores from three regions of UK blanket bog classified by restoration status (10- and 5-years post restoration, degraded, and intact).

	Minimum	Maximum	Median	*n =*
All	-32.19	-0.01	-2.61	443
10Y	-26.59	-0.27	-3.00	110
5Y	-32.19	-0.26	-3.15	112
Degraded	-29.4	-0.01	-0.86	107
Intact	-28.85	-0.06	-3.35	114
Exmoor	-32.19	-0.13	-4.22	145
The Peak District	-15.81	-0.01	-2.49	143
Scotland	-14.93	-0.11	-2.22	155

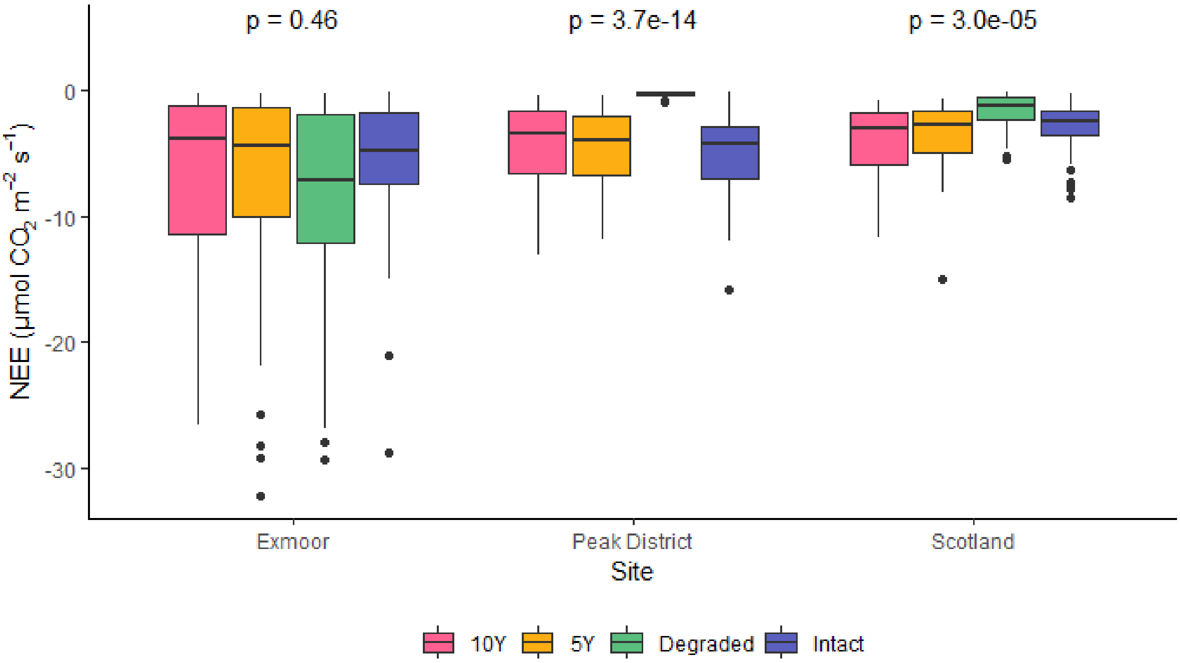


Figure 5.23 Net ecosystem exchange of mesocosm cores from three regions of blanket bog in the UK classified by restoration status (10- and 5-years post restoration, degraded and intact). Statistical testing results shown. Outliers shown beyond the whiskers.

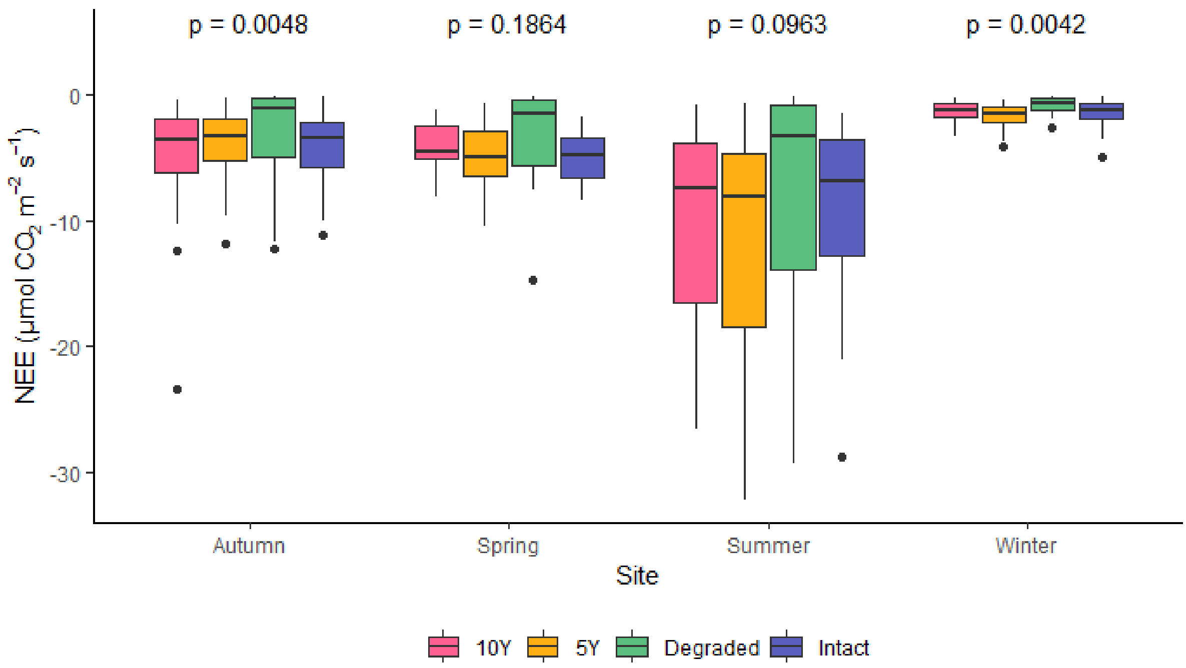


Figure 5.24 Seasonal variation in net ecosystem exchange of mesocosm cores from three regions of blanket bog in the UK classified by restoration status (10- and 5-years post restoration, degraded and intact). Statistical testing from Kruskal-Wallis results shown. Outliers shown beyond the whiskers.

5.3.4.3 Ecosystem respiration (R_{eco})

R_{eco} ranged from 0.03 µmol CO_2 m^{-2} s^{-1} to 17.13 µmol CO_2 m^{-2} s^{-1} with a median of 2.39 µmol CO_2 m^{-2} s^{-1}. R_{eco} was significantly lower in degraded cores compared to other RS (KW chi-squared = 47.71, df = 23, $p < 0.01$; post-hoc $p < 0.01$), largely reflecting differences at the Peak District but also at Scotland. Median R_{eco} was significantly higher in cores from Exmoor compared with cores from the Peak District and Scotland (KW chi-squared = 27.55, df = 2, $p < 0.01$). At the site level, there was no difference in R_{eco} between RS in Exmoor cores, but in cores from the Peak District and Scotland, R_{eco} was significantly lower in degraded cores (post-hoc $p < 0.05$; Figure 5.25). There was significant variation in R_{eco} seasonally (Figure 5.26) with fluxes being lowest in winter (median 0.66 µmol CO_2 m^{-2} s^{-1}) and highest in summer (median 6.46 µmol CO_2 m^{-2} s^{-1}) and R_{eco} was significantly correlated with chamber temperature ($R = 0.55$, $p < 0.01$). Seasonally, fluxes from cores of each RS differed significantly with the lowest fluxes being measured in degraded cores and the highest fluxes from either 10Y or 5Y cores. R_{eco} was not significantly correlated with % vegetation coverage for any species and there was no significant difference in flux when cores were classified by the dominant vegetation group.

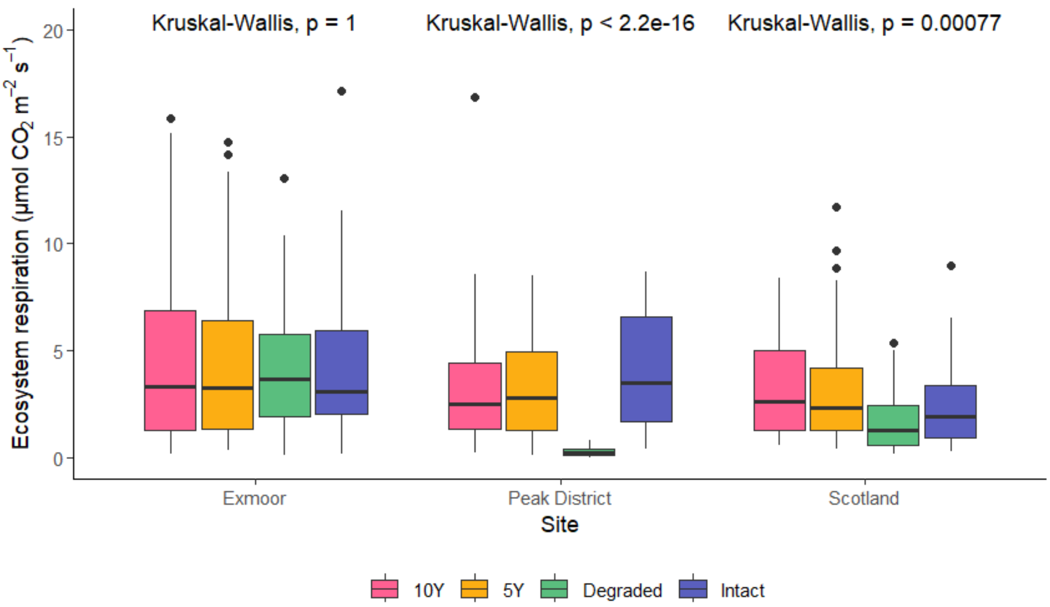


Figure 5.25 Ecosystem respiration (R_{eco}) of mesocosm cores from three regions of blanket bog in the UK classified by restoration status (10- and 5-years post restoration, degraded and intact). Statistical testing results shown. Outliers shown beyond the whiskers.

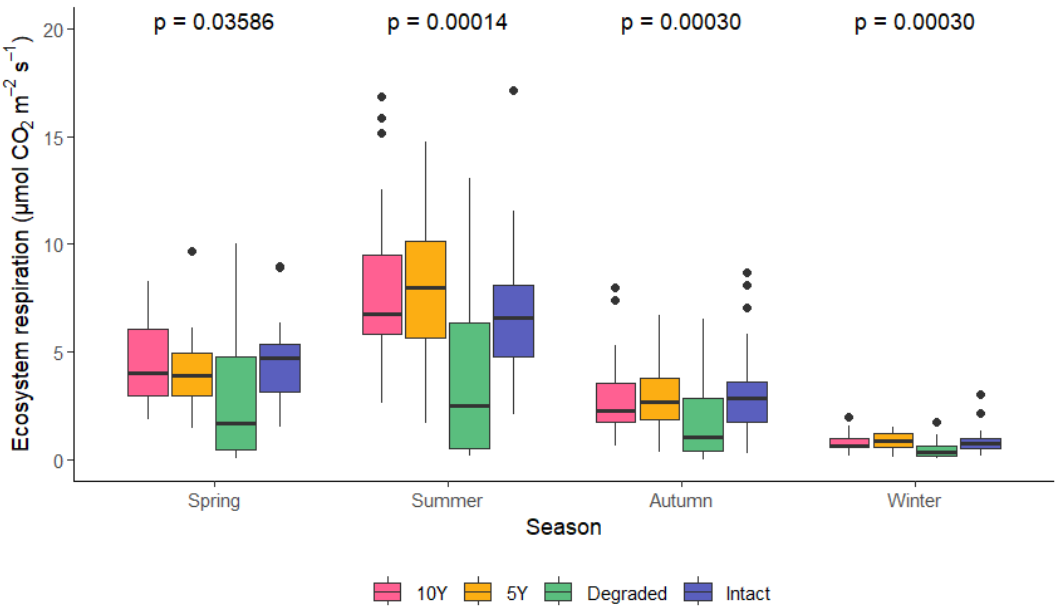


Figure 5.26 Seasonal ecosystem respiration (R_{eco}) of mesocosm cores from three regions of blanket bog (Exmoor, the Peak District, and Scotland) in the UK classified by restoration status (10- and 5-years post restoration, degraded and intact). Kruskal-Wallis statistical testing results are shown. Outliers shown beyond the whiskers. Spring = March, April, and May; Summer = June, July, and August; Autumn = September, October, and November; Winter = December, January, and February.

5.3.4.4 *Methane fluxes (CH_4)*

In full light conditions, CH_4 flux ranged from -158.92 to 259.50 nmol CH_4 m^{-2} s^{-1} with a median of 6.56 nmol CH_4 m^{-2} s^{-1}. There was a significant difference in fluxes when comparing RS (KW chi-squared = 66.07, df = 3, $p < 0.001$) with intact cores showing the highest median flux (12.62 nmol CH_4 m^{-2} s^{-1}) and degraded cores having the lowest (0.45 nmol CH_4 m^{-2} s^{-1}). Intact cores have significantly higher CH_4 fluxes than all other RS cores (post-hoc $p < 0.01$). Cores from the Peak District had significantly lower fluxes compared to cores from Exmoor and Scotland (KW chi-squared = 70.181, df = 2, $p < 0.001$, post-hoc $p < 0.01$). Within site differences (Figure 5.27) showed intact cores having higher fluxes in cores from Exmoor and the Peak District, however 10Y and 5Y cores from Scotland had a higher flux compared to degraded and intact cores. CH_4 flux was significantly correlated with % coverage of herb ($R = 0.14$, $p < 0.01$), *Sphagnum* ($R = 0.21$, $p < 0.01$), and bare peat ($R = -0.18$, $p < 0.01$). CH_4 flux and porewater pH were tested for correlation where a porewater collection accompanied gas flux measurements and were found to be significantly positively correlated albeit with low correlation coefficient ($R = 0.14$, $p < 0.05$).

CH_4 flux differed significantly on a seasonal basis (KW chi-squared = 46.966, df = 3, $p < 0.01$; post-hoc $p < 0.01$) with median flux being highest in summer (19.81 nmol CH_4 m^{-2} s^{-1}) and lowest in winter (2.03 nmol CH_4 m^{-2} s^{-1}) as CH_4 flux was significantly correlated with temperature ($R = 0.27$, $p < 0.01$). Fluxes from degraded cores was lowest in each season and in cores from Exmoor and the Peak District, intact cores had the highest flux (Figure 5.27).

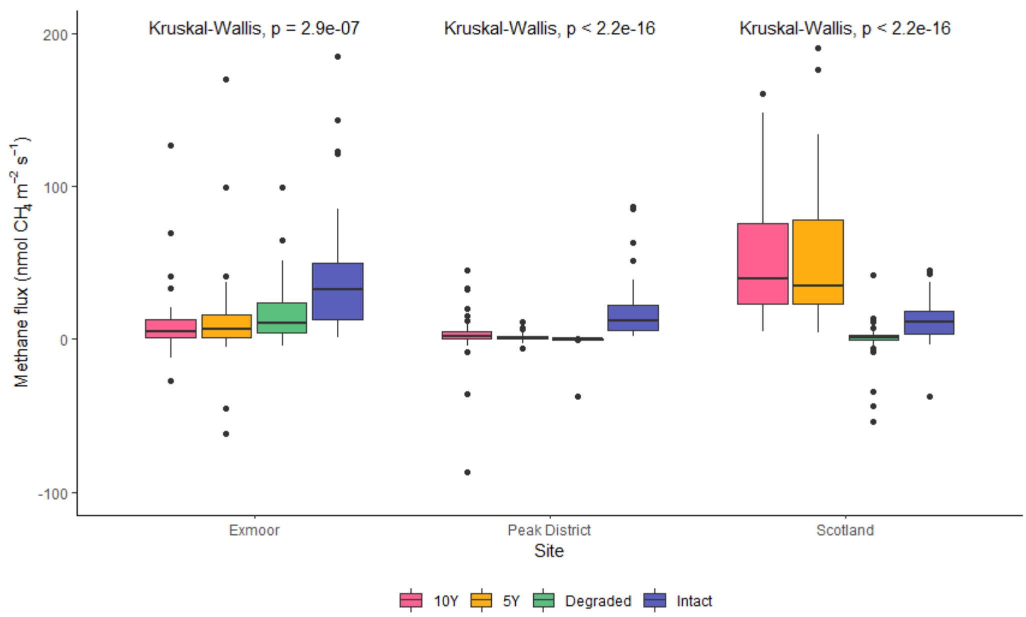


Figure 5.27 Soil methane flux (nmol CO_2 m^{-2} s^{-1}) of mesocosm cores from three regions of blanket bog in the UK (Exmoor, the Peak District, and Scotland) classified by restoration status (10- and 5-year post restoration, degraded, and intact). Significance testing for within site differences shown. 6 outliers removed according to three sigma error as detailed in methodology. Spring = March, April, and May; Summer = June, July, and August; Autumn = September, October, and November; Winter = December, January, and February.

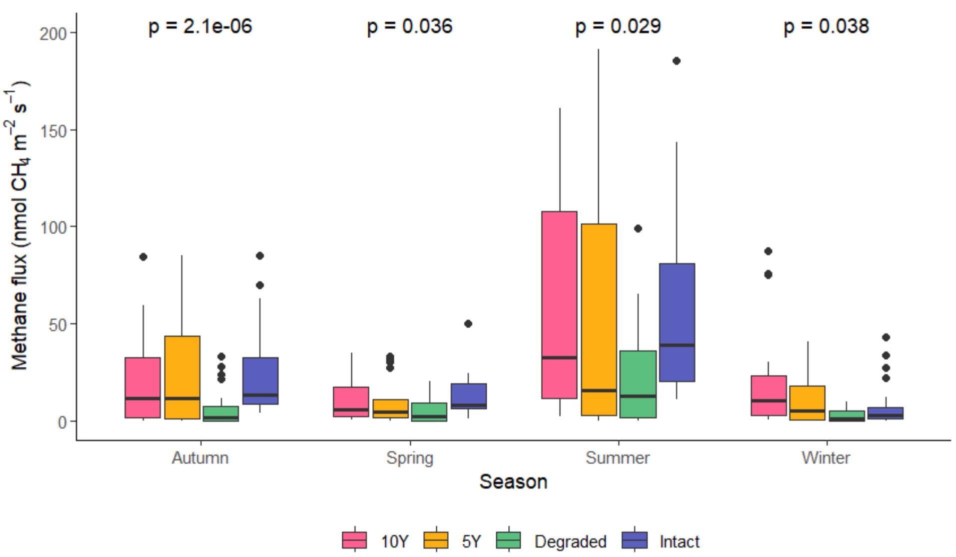


Figure 5.28 Seasonal soil methane flux (nmol CO_2 m^{-2} s^{-1}) of mesocosm cores from three regions of blanket bog in the UK (Exmoor, the Peak District, and Scotland) classified by restoration status (10- and 5-year post restoration, degraded, and intact). Significance testing result shown.

5.3.5 Results summary

Significance test results for water quality and GHG flux between restoration status, sites, and within site differences as reported in this chapter are summarised in Table 5.18.

Table 5.17 Summary of p values obtained from statistical analysis of differences in key vegetation groups and water quality parameters and gas fluxes (net ecosystem exchange, ecosystem respiration, soil respiration (NEE in full light, R_{eco} in the dark, SR with roots respectively) and methane flux) between site, restoration status. p values in bold indicate a significant difference (significant level $p \leq 0.05$).

	DOC	TbN	$SUVA_{254}$	Hazen	pH	% *C. vulgaris*	% *Sphagnum*	% Sedge	% Brash
Site	**p < 0.05**	**p = 0.02**	**< 0.001**	**< 0.001**	**p < 0.05**	**p < 0.001**	**p < 0.001**	**p = 0.04**	**p < 0.001**
Restoration status	**p < 0.05**	**p < 0.001**	**p = 0.04**	**p < 0.01**	**P = 0.03**	**p < 0.001**	**p < 0.001**	**p < 0.001**	**p < 0.001**
	NEE	R_{eco}	SR	Methane					
Site	**p < 0.05**	**p < 0.01**	**p = 0.04**	**p < 0.01**					
Restoration status	**p < 0.01**	**p < 0.01**	**p = 0.007**	**p < 0.01**					

5.4 Discussion

The aim of the restoration of degraded peatlands is commonly to re-establish ecosystem functioning (Gorham and Rochefort, 2003), returning peatland hydrology, geochemical cycling, and C fluxes to that found in intact blanket bog. Due to the state of UK peatlands and the limited area of what can be considered intact, what this means in practice is not clear. Largely, this centres around raising water tables to prevent aerobic decomposition of peat OM with the re-introduction of *Sphagnum* considered essential to return blanket bog back to an active and functional state (Rochefort, 2000). In this study, *Sphagnum* moss was most significantly associated with intact mesocosm cores as well as those from Scotland. Often considered a keystone species in blanket bog ecosystems (McCarter *et al*., 2021), *Sphagnum* mosses are significant in the formation of peat (Breeman, 1995) and the regulation of water quality (Armstrong *et al*., 2012; Ritson *et al*., 2016) but require wet conditions for propagation and growth (Rosenburgh, 2015).

Raising water tables via rewetting can support *Sphagnum* regeneration whilst also increasing near-surface soil moisture (Price and Whitehead, 2001). A high % coverage of *Sphagnum* defines such sites an 'active' blanket bog (i.e., peat forming; JNCC, 2004, 2009), although definitions of habitat status are questionable (Davies *et al*., 2016). Moreover, rewetting claims often lack evidence and represent a too simplistic view on peat-forming species (i.e. many species form peat, not just *Sphagnum* moss) and lack consideration of site-specific limitations in potential wetness (see Ashby & Heinemeyer, 2021). However, mean *Sphagnum* coverage was lowest on degraded cores, and subsequently increased from 5Y to 10Y to intact cores, whilst bare peat % coverage was highest in degraded cores and decreased from 5Y to 10Y to intact cores. This suggests that restoration (which on the sites studied is largely by ditch blocking and rewetting) is beneficial with regards to vegetation community composition and aids a shift from bare peat (which is more vulnerable to erosion) to a wetter condition which promote *Sphagnum* growth.

Whilst the change in *Sphagnum* cover indicates a restoration induced shift in vegetation to a more desired (i.e., *Sphagnum* dominant) state, it is important to note that degraded cores were largely characterised by a high coverage of bare peat. Peak District degraded cores had a mean bare % coverage of 96.7 ± 23.46 % and Scottish degraded cores had a mean bare coverage of 32.61 ± 35.61 %. Bare peat can lead to increased rates of soil erosion through freeze-thaw mechanisms, desiccation, and wind action (Rosenburgh, 2015). In the Pennines (i.e, the Peak District), wind erosion was estimated to occur > 47 days in a year and increases with altitude (Bower, 1961). Degraded cores were collected from an altitude of 522 to 615 m and thus, erosion is likely to be a significant process by which degradation occurred. Moreover, southern Pennine blanket bogs have been subject to historic, prolonged atmospheric pollution due to heavy pollution deposition (Rosenburgh, 2015). *Sphagnum* mosses lack a cuticle which in other plant species provides protection from atmospheric deposition, which in this location would include phytotoxic metals (Rosenburgh, 2015). Elemental analysis on the peat samples utilised in this study as reported by Burn (2022) showed that peat soil concentrations of metals was not significantly higher in samples from the Peak District compared to other regions of blanket bog. However, as this area was severely eroded, it is likely that metal enriched peat led was eroded and subsequently released into aquatic systems (Rothwell *et al*., 2005).

In the context of restoration, degraded, bare areas of peat represent a significant challenge. The recolonisation of vegetation-devoid peat surfaces by *Sphagnum* mosses is considered one of the most significant challenges faced in peatland restoration (Campeau and Rochefort, 1996). Whilst discussed in the context of peat harvesting, it has been noted bare peat is more likely to be recolonised by ericaceous shrubs rather than more desirable peatland vegetation such as *Sphagnum* moss (Campeau and Rochefort, 1996). In the context of this study, it has been demonstrated that this has implications for ecosystem service delivery – cores from Exmoor which were dominated by *Molinia* grasses showed higher SR and R_{eco} fluxes and a lower $SUVA_{254}$ which may be problematic in the context of drinking water treatment.

It is also important to consider a site's potential for rewetting and achieving a *Sphagnum* rich vegetation community. In the context of restoration, differences in natural wetness for different types of blanket bog and peatlands is important, especially when comparing naturally drier 'typical' hill blanket bog versus naturally wetter raised bogs (Glatzel *et al*., 2023) or topogenous bogs (Wheeler *et al*., 2020; 2023). Such considerations around habitat status and restoration potential also have implications for the delivery of ecosystem services such as drinking water provisioning and C storage, likely due to influences on water table depth, soil temperature and vegetation (Armstrong *et al*., 2012; Davies *et al*., 2016; Dixon *et al*., 2015; Harper *et al*., 2018)

5.4.1 Water Quality

The reduction of DOC production and export, along with water colour is an important motivation for peatland restoration, particularly in the UK where a significant portion of drinking water originates in peatland-dominated catchments (Xu *et al*., 2018). Utility companies are increasingly seeking alternative methods to treating drinking water to reduce coagulant demands and DBP production (Ritson *et al*., 2016). Many studies have focussed on ditch blocking; however, this may not be a suitable or effective restoration method for all degraded peatlands, and not all peatlands have been drained and naturally experience drier periods (Ashby & Heinemeyer, 2021; Bellamy *et al*., 2012). Parry *et al*., (2014) report that whilst generally ditch blocking leads to a reduction in DOC concentration and export, the sampling strategies and DOC monitoring techniques in these studies vary. As different temporal and spatial scales are assessed within these studies, comparisons between results is difficult and in addition, the longest monitoring time scale extends to only 9 years (Worrall *et al*., 2022). This study used a space-for-time design, but as mesocosms were kept under the same conditions in York, it allowed for a comparison of water quality in blanket bog of varying habitat condition from degraded to restored to intact. It was hoped that it can improve our understanding of how restoration benefits water quality and thus drinking water provision.

GLM (Table 5.9) indicated that the significant drivers of DOC concentration were air temperature, DON concentration and % grass coverage. The seasonal cycle (and thus temperature) has an important role in the seasonal fluctuations in DOC production and export and seasonal variation in DOC may arise from increased plant rhizodeposition and soil microbial activity (Bonnett *et al*., 2006). This may also be a mechanism to explain differences between DOC concentration in cores from Scotland and Exmoor however, disentangling climate effects from differences in vegetation community is difficult. *Molinia* grass leads to a reduction in DOC concentration due to drawdown of the water table. This introduction of oxygen leads to increased decomposition of OM, reflected in the lower porewater DOC concentrations (Figure 5.10) and higher SR fluxes (Figure 5.21). A second GLM was ran, excluding Exmoor data from the analysis. This was because Exmoor cores were largely dominated by *Molinia* grass which is known to have significant influence on peat geochemical processes (Leroy *et al*., 2018; Meade, 2015). This GLM (Table 5.10) identifies air temperature, pH, and % shrub and brash coverage. Shrub roots are a significant input of C in peat soils (Zeh *et al*., 2019) and the positive correlation between % brash coverage and DOC concentration is likely due to brash decomposition.

It was expected the water quality in porewaters from degraded cores would be lower than that of the restored and intact cores, however this was not the case. Degraded cores characterised by bare peat showed lower DOC concentrations and UV absorbance compared to their intact counterparts, likely due to little to no fresh OM soil inputs to be exploited by soil microbial communities (Aguilar and Thibodeaux, 2005). Degraded cores dominated by bare peat also had the lowest median SR (Figure 5.21 and R_{eco} fluxes (Figure 5.25), and highest NEE fluxes (Figure 5.23).

Median DOC concentrations and UV_{254} absorbance were significantly higher in intact cores. However, when UV_{254} absorbance was corrected for DOC concentration ($SUVA_{254}$), there was no difference between RS. This suggests that the nature of the DOC does not differ between restoration status. 10Y cores at all sites have a higher median DOC concentration compared to degraded cores which may be linked with the flushing of soil upon raising the water table following restoration (Fenner and Freeman, 2011). An increase in SUVA post-restoration (i.e., degraded to 10Y) may be due to a change in DOC source as it is darker suggesting it is more recalcitrant. This may be due to short-term disturbances to the peat soil which enables the mobilisation of deeper, older C into aqueous systems (Gatis *et al*., 2023). At some locations, elevated DOC concentrations with higher aromaticity have persisted following restoration (Yu, 2012).

When considering mesocosm core dominant vegetation group, cores dominated by grass (i.e., *Molinia caerulea*) had significantly lower $SUVA_{254}$, which suggests that the non-UV_{254}-absorbing OM fraction constitutes a higher portion of the DOC compared to other cores. This fraction includes compounds such as amino acids and proteins which do not absorb within the wavelength ranges tested. These are problematic in the context of water treatment given that they are not amenable to coagulation, and thus represent a source of potential DBP precursors. The encroachment of vascular plants onto blanket bog has been reported following periods of degradation (Voigt *et al*., 2024), and thus peatland degradation represents a mechanism by which DBP precursor load in waters entering WTWs may increase.

GLM modelling was undertaken to determine the significant drivers in differences in UV_{254} absorbance (Table 5.14). DOC concentration, % grass, and % bare peat coverage were identified as significant drivers of UV_{254} absorbance. UV_{254} absorbance was positively correlated with DOC concentration which was expected given that a higher DOC concentration means a more UV_{254} absorbing chromophores. Bare ground coverage was also positively correlated with $SUVA_{254}$ which is likely due to a very low/non-existing turnover of OM due to the severe degradation of the degraded Peak District cores which have ~ 100 % bare coverage for the duration of this study. The previously (i.e., at their natural location) low water table depths (Evans and Shuttleworth, 2016) means that a higher portion of the soil column is aerobic and thus, there has been preferential utilisation of the more labile OM leading to a build-up of more recalcitrant compounds which persist in the soil. The % grass coverage was negatively correlated with UV_{254} absorbance which is likely due to the rapid turnover of OM in *Molinia* dominated peatlands and low water tables due to root drawdown. Cores dominated by grass also had a lower median DOC concentration compared to other vegetation groups meaning less DBP precursor material.

Restoration did not have a significant positive impact upon water quality. DOC was found to increase following restoration however this increase was non-significant (Gatis *et al*., 2023). Colour and SUVA also increased since restoration indicative of more recalcitrant, darker DOC (Gatis *et al*., 2023). Whilst higher DOC concentrations may increase the chemical demand of a raw water during water treatment, hydrophobic DOC is readily removed during coagulation and thus may not represent a significant source of disinfectant by-product precursors. In addition, more recalcitrant DOC represents a more stable component of the peatland C pool than more labile C, and thus, may be beneficial when considering long-term C storage.

Without understanding DOC exports from peatlands in pristine condition, caution should be taken when relying on peatland restoration for improvements in water quality. This study only considers up to 10 years post restoration, and therefore, it may be possible that a greater time since restoration is needed before these improvements to peatland functioning is reflected with an improvement in water quality. Longer term studies (i.e., 20 + years) are needed to give insight into realistic timescales and trajectories for improvements to DOC concentrations and water colour following restoration (Gatis *et al*., 2023).

5.4.2 Soil properties

The movement of water through the peat matrix is a significant control on the biogeochemistry and physical characteristics of a peat soil (Ours *et al*., 1997; Rezanezhad *et al*., 2016). Degradation by drainage leads to drying and pore collapse and thus compaction, increasing bulk density, and reducing the soils water holding capacity. It can also cause a loss of the preferred pore orientation, and hence a decrease in anisotropy (Beckwith *et al*., 2003), which may be associated with higher BD. In this study, degraded cores had the highest median BD as well as the lowest median SM at each site. Increased BD reduces water availability to vegetation, particularly mosses which rely on passive capillary transport (Sagot and Rochefort, 1996; Noble *et al*., 2017). A higher BD is associated with increased OM decomposition which is reflected in higher C:N measured in degraded peat samples in this study.

Peat soil hydraulic properties largely depend upon peatland vegetation and the degree of decomposition of plant litter and OM (Rezanezhad *et al*., 2016). Currently, the effects of vegetation on BD is understudied but Folking *et al* (2010) attempted to include vegetation coverage in peat accumulation models which considered BD. Peat BD was considered a function of humification and influenced both the growth of the peat column (and C sequestration), and hydraulic conductivity. The proportion of large pores within a peat soil is affected by peat decomposition as the breakdown of soil and plant OM reduces the inter-particle pore spaces (Bragazza *et al*., 2009; Moor *et al*., 2005). Peat that has undergone a lesser degree of decomposition has higher plasticity which enables it to expand and contract upon wetting and drying. A higher C:N in degraded cores suggests a greater degree of decomposition, accompanied by lower active porosity and compressibility (Rezanezhad *et al*., 2016). This may be problematic following periods of drought and heavy rainfall. Thus, degraded peatlands may be less resilient with future climate warming.

5.4.3 Gas fluxes

The restoration of blanket bog in the UK is largely focussed on raising water tables due to associations with ecosystem service provisioning (Armstrong *et al*., 2009). Soil saturation slows the microbial decomposition of plant litter and OM (Loisel and Gallego-Sala, 2022) which may have benefits for C fluxes including increased photosynthesis and thus C uptake (Dixon *et al*., 2014). However, this may come at the expense of higher CH_4 fluxes (Huttunen *et al*., 2003). Following degradation, blanket bog may become a C source due to increased mineralisation when the water table is lower (due to enhanced OM decomposition), and a source of CH_4 during periods of inundation (Tiemeyer *et al*., 2016). This work aimed to provide insight into GHG fluxes and peatland C balance in the context of restoration.

SR_{uncut} was significantly higher in cores from Exmoor compared to Scotland which was likely due to the higher *Molinia* coverage on degraded cores. *Molinia* can develop extensive root systems due to the and thus, can exploit large volumes of soil (Taylor *et al*., 2001). For all sites, 5Y cores had a higher flux compared to degraded and 10Y cores which could be attributed to disturbance following restoration. SR in degraded cores from the Peak District was the lowest of all core groups, which is likely due to 100 % coverage of bare peat.

Median NEE was highest on degraded cores meaning less C was being absorbed in these systems. In cores from Scotland and the Peak District, degraded cores had significantly higher NEE compared to other restoration status' however, this was not seen at Exmoor. This is likely due to vegetation community composition being similar between restoration status' at Exmoor, whilst on cores from the other sites, this differs. Intact cores from Scotland and the Peak District had lower NEE fluxes (i.e, absorbing more C; Figure 5.23) compared to restored cores, which is likely due to higher decomposition due to disturbance. Revegetation following restoration will stimulate both autotrophic and heterotrophic components of ecosystem respiration along with increasing soil microbial biomass (Dixon *et al*., 2014). Vegetation on previously bare peat will therefore increase GPP, however, to what degree largely depends upon site conditions and vegetation present (Ward *et al*., 2009). Hambley *et al* (2018) reported that near intact and older restored sites (16Y) had more negative NEE compared to a more recently restored site (10Y) which had a positive NEE, again supporting that restoration success needs to be assessed over longer time periods. In this study, restored cores were significantly associated with *C. vulgaris* and brash coverage. Brash represents an input of OM into peat soils, thus increasing rates of decomposition. Lower water tables under areas dominated by *C. vulgaris* also enhance R_{eco}. There has been substantial work into the impacts of *C. vulgaris* management on ecosystem service delivery (as discussed in Chapter 4) and is also an important consideration in restoration practices. A higher heather canopy height has been shown to lead to a more positive NEE as the amount of photosynthesis per unit of respiration decreases (Dixon *et al*., 2015). Lower water tables under areas dominated by *C. vulgaris* also enhance R_{eco} contributing to increased NEE.

CH_4 fluxes were shown to differ significantly between restoration status with intact cores having the highest median flux, and degraded cores having the lowest (Figure 5.27). This may be attributed to an in-field higher water table (Huttunen *et al*., 2003) and represents a memory effect linked to microbes. A study on an Irish lowland blanket bog showed that water table was the most significant driver of spatial variations in mean flux rate and where there was a persistently high-water table, vegetation community composition was also a strong indicator (Laine *et al*., 2007). CH_4 flux was positively correlated with *Sphagnum* (which was significantly associated with intact cores (Table 5.2)) coverage, which again supports the observation that a higher water table depth leads to an increased CH_4flux (Turetsky *et al*., 2008). Higher CH_4 fluxes have also been reported by Gatis *et al* (2023) area where rewetting has occurred (albeit on a 0-4 years' timescale) and in a study by Strack *et al* (2016), CH_4 emissions were significantly higher in restored plots compared to degraded plots but were significantly lower on average compared to intact plots. Bare peat coverage was negatively correlated with CH_4 flux which is attributed to the lack of vegetation. Other studies reported a significant correlation with CH_4 flux and pH, and whilst a significant correlation was reported in this study, the R value was relatively low.

GHG fluxes differed significantly seasonally (Figure 5.24 and Figure 5.26) and were significantly positively correlated with temperature which has implications under future climate projections. Higher temperatures and altered precipitation patterns (Wilson *et al*., 2016) can accelerate decomposition in peat soils due to increased oxygen availability (Drzymulska, 2016), often resulting in increased C fluxes (Maljanen *et al*., 2010). Whilst drying could be considered beneficial in the context of CH_4 fluxes (drier conditions lead to a reduction in CH_4 flux (Maljanen *et al*., 2010), *Sphagnum* growth could be impeded, leaving sites vulnerable to the encroachment of vascular plants such as *Molinia* grasses (as seen in Exmoor cores in this study; (Voigt *et al*., 2024)). Wetter conditions should promote the re-establishment of more typical peatland communities, sometimes combined with further interventions such as *Sphagnum* planting (Hugron *et al*., 2020; Gatis *et al*., 2023).

Peatland restoration has been shown to increase gaseous C uptake (Nugent *et al*., 2018). These increases are most significant where restoration increases vegetation coverage due to increased photosynthesis (Gatis *et al*., 2023) i.e., revegetation on previously bare and exposed peat (Clay *et al*., 2012). Considering this, degraded sites from the Peak District which were sampled in this study offer a significant restoration opportunity due to high bare peat coverage. Raising water table depths would decrease gaseous carbon losses, with any increase in CH_4 offset by a reduction in the NEE (Clay *et al*., 2012; Dixon *et al*., 2014; Nugent *et al*., 2018). Raised water tables would also reduce the production of DOC and gaseous C by soil decomposition (as measured by heterotrophic respiration), reducing aquatic carbon losses, thereby improving water quality. Generally, within the literature, rewetting is assumed to lead to a net positive impact (Ashby and Heinemeyer, 2021). It has been suggested that raised water tables may lead to saturated overland flow and potentially exacerbate downstream flooding (Acreman and Holden, 2013). However, in the case of the Peak District degraded cores featured in this study, raising water tables may be important in reducing bare peat coverage and promoting the growth of desirable blanket bog vegetation communities such as *Sphagnum*.

5.5 Conclusion

Using seasonal mesocosm porewater sampling and GHG flux measurements, this study has shown large scale differences in water quality and gas emissions between blanket bog restoration status and UK sites. Sites which were considered intact were significantly associated with higher *Sphagnum* coverage whilst degraded sites were significantly associated with higher coverage of bare peat (however it is important to note that this was largely due to the degraded Peak District sites which were characterised by a landscape of bare, eroding peat). This study has also shown that the delivery of the benefits of restoration and rewetting are site specific. Cores from Exmoor showed no significant differences in DOC concentration or colour between restoration status and samples showed significant differences to other sites which is likely due to a high *Molinia* coverage.

Hypothesis 1 stated that that water quality in intact cores was predicted to be higher than in degraded cores. This was shown to be incorrect due to higher DOC concentrations and higher colour (UV_{254} absorbance and hazen) in intact cores. However, high colour indicates that DOC is more amenable to coagulation and whilst the higher DOC loading means a higher coagulant demand and higher associated costs, DOC from such sites may not prove a significant risk in the context of disinfectant by-product formation. Hypothesis 2 stated that degraded cores would be a C source whilst intact cores would be a C sink, and this would be linked to vegetation cover. This was not proven to be correct. Whilst median NEE for degraded cores was higher, it was still a negative flux. As cores from the Peak District had no vegetation, this reduced C uptake (in the case of photosynthesis) and thus had lower R_{eco} and CH_4 fluxes. Whilst for cores from Scotland this was true, degraded cores from Exmoor had similar fluxes compared to intact cores, and therefore it is likely that this was dependent on vegetation and site-specific features. Hypothesis 3 stated that vegetation and water table depth were the most significant drivers of water quality and GHG fluxes. GHG fluxes and WQ parameters were shown to be significantly affected by overlying vegetation community and there was significant seasonal variation in both water quality parameters and GHG fluxes. As water table depth and temperature were significantly correlated, it is difficult to establish which exerted a more significant control, and thus, it is likely both were significant drivers of differences in both water quality and GHG fluxes.

The degradation of peatlands through mismanagement is currently responsible for 5-10% of the global annual anthropogenic CO_2 emissions (Loisel and Gallego-Sala, 2022). Effective restoration should therefore be a priority in climate change mitigation efforts. However, many published studies only monitored progression following restoration for a short period (in some cases for only 4 years e.g., Gatis *et al* (2023)) and this study has demonstrated that even 10 years is not a sufficient time to see restoration benefits. It also needs to be recognised in studies that some bogs (such as topogenous bogs) are naturally drier and therefore may naturally differ in vegetation community composition.

In addition, to improve understanding of the impacts of restoration upon ecosystem service delivery in peatland ecosystems, more Before-after-control-impact (also known as BACI) studies are needed to compare conditions prior to- and following- restoration with regular monitoring. This is especially important because the same restoration methods do not achieve the same outcome on all sites (Parry *et al*., 2014). Comparing the response of different vegetation types to restoration under similar climatic conditions would also be useful to determine if and how, we can ensure that following restoration, vegetation community composition is in a 'desired' state. Whilst restoration is a crucial step in halting peatland degradation, it is imperative that the potential outcomes are well understood by both practitioners and policymakers and on what timescales these outcomes are expected to come to fruition (Gatis *et al*., 2023).

6 Climate and blanket bog ecosystem provisioning

6.1 Chapter summary

Blanket bogs have historically been C sinks however under climate warming projections, C balance is expected to shift leading to destabilisation of soil C stocks. Projections of blanket bog functioning under climate change have been contradictory, and this study aimed to improve understanding of how climate may impact DOC concentration and composition, and peatland GHG which is important for delivering effective future management. Seasonal porewater collections and GHG flux measurements were taken from mesocosm cores from four regions of blanket bog under different climatic conditions to investigate the role of climate in C fluxes. Temperature was shown to exert a significant control fluxes and water quality with higher temperatures leading to increased DOC concentration and colour (UV_{254} and UV_{400} absorbance). The warmest site was dominated by Molinia and was associated with a lower DOC concentration but with a DOC composition that is less amenable to water treatment compared to the cooler sites. It is difficult to disentangle the effects of climate and vegetation community composition upon water quality and GHG fluxes and there were likely ‘memory effects’ of in-situ climate whereby microbial communities reflected region climatic conditions. To further understanding, results from this work could be coupled with microbial community analysis to further understand interactions between soil biota, vegetation, and hydrological processes occurring within peat soils.

6.2 Introduction

(Wilson *et al*., 2016). .Historically, blanket bogs have been C sinks as C-fixation rates have exceeded the rate of heterotrophic decomposition. However, under predicted future warming conditions and alterations to hydrological regimes (Wilson *et al*., 2016) this balance is likely to shift due to higher heterotrophic respiration rates and increased decomposition. This shift may result in the release of long-term stored C as CO_2 and CH_4 (Baysinger *et al*., 2022; Salimi and Scholz, 2021), leading to a subsequent destabilisation of peat soil C stocks with some peatlands becoming net C sources (Leifield *et al*., 2019).

In the UK, historically, blanket bog has undergone intensive management (Reed *et al*., 2009) which has led to long-term degradation, and in some cases, a decline in blanket bog area. Subsequently, reversal of this is degradation and area decline is now the focus in much of the blanket bog management and restoration being undertaken (Parry *et al*., 2014). Whilst this is certainly valuable (especially in the context of water quality and water treatment as discussed in this thesis), climate has been identified as the more significant driver in blanket bog distribution and functioning when compared to land-use history (Gallego-Sala *et al*., 2016). It is predicted that climate change will affect a large portion of blanket bog within the next century which will make blanket bog more vulnerable to degradation via other mechanisms (Clark *et al*., 2010; Gallego-Sala *et al*., 2010; Gallego-Sala and Prentice, 2013). It is understood that water table depth and temperature are significant controls over peat soil C processes (Dixon *et al*., 2014; Hilasvuori *et al*., 2013; Wilson *et al*., 2016) and thus, changes to either/both is likely to alter processes upon which long-term C sequestration and stabilisation relies (Wilson *et al*., 2016). Therefore, altered precipitation patters and more frequent and prolonged droughts may destabilise the long-term C pool (Evans and Warburton, 2010; Fenner and Freeman, 2011a).

Many studies have focussed on surface warming and therefore, there is limited understanding of the effects of rising temperatures of C stocks further down the peat column (e.g., in the catotelm). Deep heating of the peat column increase CH_4 emissions however the authors attributed this to surface processes and not degradation of catotelm peat. Radiocarbon analyses demonstrate that CH_4 and CO_2 are produced primarily from decomposition of surface-derived modern photosynthate, not catotelm C. Results suggest that although surface peat will respond to increasing temperature, the large reservoir of catotelm C is stable under anoxic conditions (Wilson *et al*., 2016).

Considering this, the aims of this controlled mesocosm study were to assess how differences in climate (i.e., temperature and precipitation) impact ecosystem service delivery (i.e., water quality, C storage, and GHG emissions). Therefore, the overarching research question for this chapter was *'Will climate warming affect water quality in the context of drinking water treatment, and C fluxes in the context of carbon storage and climate regulation in UK blanket bog ecosystems?'.*

As explained in more detail in Chapter 3, mesocosm cores were taken from across a climatic gradient ranging from the South to the North of the UK. This work can be considered as a Space-For-Time (SfT) study whereby climatic conditions at Exmoor represent a likely future scenario for UK blanket bog more at the edge of their bioclimatic envelope range (Gallego-Sala and Prentice, 2013). Conditions at Scottish sites represent the shrinking ideal range for blanket bog ecosystems (i.e. cool and wet). All cores were included in the analysis as the habitat status and management are reflective of the current state of blanket bog in the UK.

The hypotheses tested were as follows:

I. Blanket bog vegetation community composition changes along a climate gradient with a more *Sphagnum*-dominated vegetation community in wetter and cooler regions.

II. Water quality is best in mesocosms from the wettest and coolest sites representing slow carbon turnover and larger storage.

III. Carbon losses (CO_2) will be highest in mesocosms from the warmest and driest sites mainly due to higher respiration rates.

IV. Methane emissions will be highest in the warmest and wettest sites and in relation to plant mediated transfer in sedges.

6.3 Results

6.3.1 Climate

Annual climate data was collected for each region (i.e., each set of site locations) and is summarised in Table 6.1. Rainfall data included the total annual rainfall for 2019 (when the mesocosm cores were collected) and temperature data included both the soil and air monthly mean temperatures for the month of core collection. Exmoor was the warmest and wettest of the four regions.

Climate was investigated as a driver in differences between site vegetation cover. A PERMANOVA was undertaken on a Bray-Curtis dissimilarity matrix of vegetation found that 66 % of the variation in vegetation community composition between regions can be explained by average air and soil temperature of the month of core collection, total precipitation for the month of core collection, latitude, elevation, and management/restoration status (Table 6.2).

Table 6.1 Mean climate conditions for regional site groupings. All means shown are from 2019 and both day of- and month of- core collection shown. Highest temperatures and precipitation are shown in bold.

		Day of collection		Month of collection		
Site	Annual rainfall (mm)	Air temperature (°C)	Soil temperature (°C)	Total rainfall (mm)	Air temperature (°C)	Soil temperature (°C)
Yorkshire	1806	7.59	7.99	103.43	5.06	4.16
Scotland	1870	8.40	5.13	60.06	5.90	4.18
Peak District	1472	7.87	7.08	59.70	4.55	**6.33**
Exmoor	**3334**	**11.10**	**8.00**	**178.40**	**8.21**	5.96

Table 6.2 PERMANOVA results comparing the significance of management/restoration status and environmental variables on vegetation community composition (*C . vulgaris*, sedge, moss, grass, and bare ground % coverage).

PERMANOVA	Sum of sq.	F model	R^2	p-value
Air temperature	1.56	38.56	0.18	0.001
Precipitation	0.64	15.65	0.08	0.001
Soil temperature	0.60	14.70	0.07	0.001
Latitude	0.84	20.66	0.10	0.001
Elevation	0.52	12.84	0.06	0.001
Management/restoration status	0.97	4.79	0.10	0.001
Residuals	14	0.57	0.07	
Total	69	8.28		

6.3.2 Vegetation coverage

A NMDS (R package "vegan", Oksanen *et al*., 2022) (Figure 6.1) was performed on vegetation survey data (stress = 0.21) showing vegetation coverage (%) differed significantly between region (ANOSIM R stat = 0.47 and RMSE = 0.0001 with 9.9 K dimensions respectively). Indicator species analysis (R package "indicspecies", Cáceres *et al*., 2022) identified species most associated with region (Table 6.3). Exmoor cores were most significantly associated with grass (*Molinia*) whilst Scottish cores were most significantly associated with *Sphagnum*. *Sphagnum* coverage differed significantly between all sites (ANOVA, F = 101.1, df =3, $p < 0.001$, Post-hoc Tukey, $p < 0.05$) with median coverage in Scotland being the highest (Figure 6.2). *Sphagnum* was also found on Exmoor cores; however, this was present on a small number of cores and thus was not representative of vegetation community composition at this site. Sedge coverage was significantly higher on cores from the Peak District and Yorkshire (KW chi-squared = 17.38, df = 3, p = 0.0005, post-hoc $p < 0.05$) compared to Exmoor and Scotland (Figure 6.3).

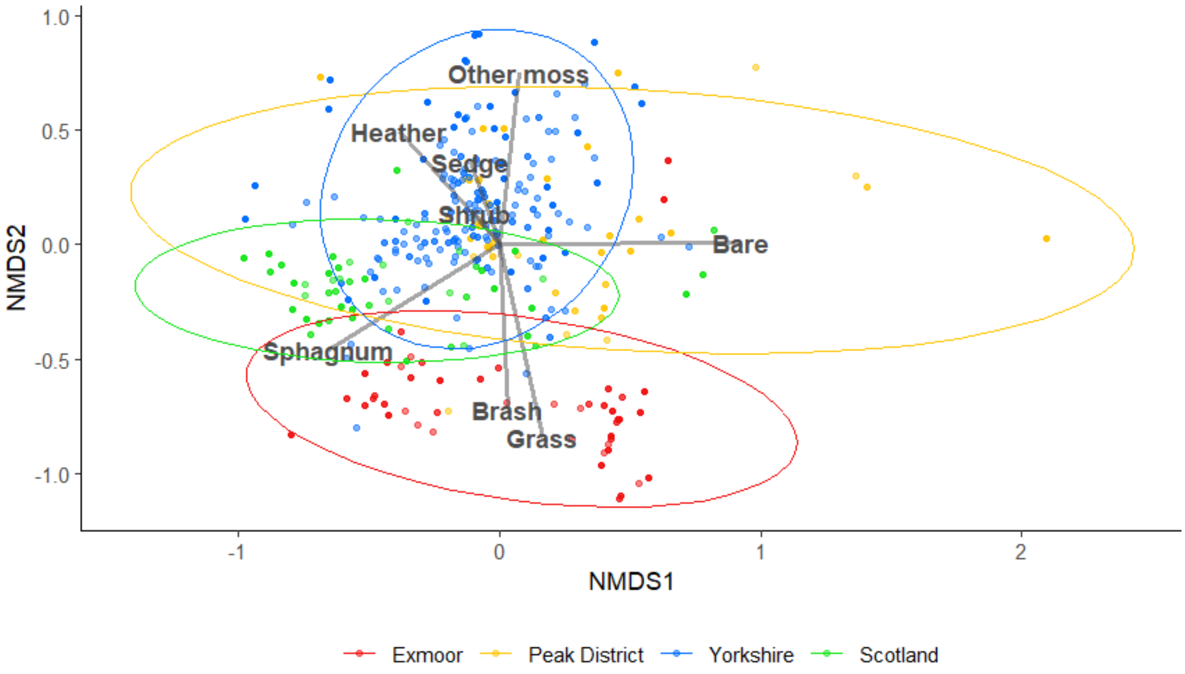


Figure 6.1 Non-metric dimensional scaling (NMDS) of vegetation groups of mesocosm central cores from four regions in the UK. Ellipses show grouping of cores from the same region. Region is indicated by colour and shape. Vegetation groups most strongly associated with regions are shown.

Table 6.3 Indicator species analysis (using R stats package "indicspecies", Cáceres *et al.*, 2022) results showing key vegetation groups most associated with each region Only significant results ($p < 0.05$) are shown. Number of iterations = 9999.

	Stat	P value
Exmoor		
Grass	0.83	< 0.001
Brash	0.24	< 0.001
The Peak District		
Bare	0.35	< 0.001
Other moss	0.51	< 0.001
Sedge	0.23	< 0.01
Yorkshire		
Heather	0.52	< 0.001
Other moss	0.51	< 0.001
Sedge	0.23	< 0.01
Scotland		
Sphagnum	0.53	< 0.001
Heather	0.52	< 0.001
Lichen	0.27	< 0.001

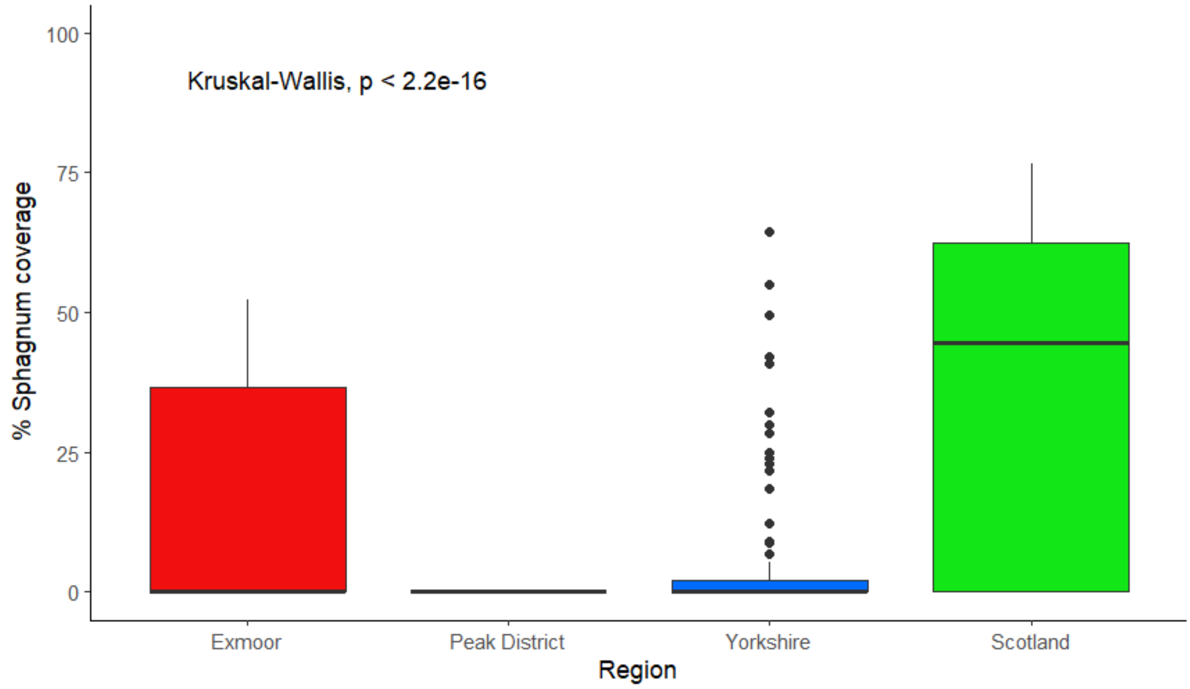


Figure 6.2 % *Sphagnum* coverage of mesocosm cores from four climatic regions. Yorkshire comprises of three distinct blanket bog sites. Outliers are shown beyond the whiskers. Statistical significance test result shown.

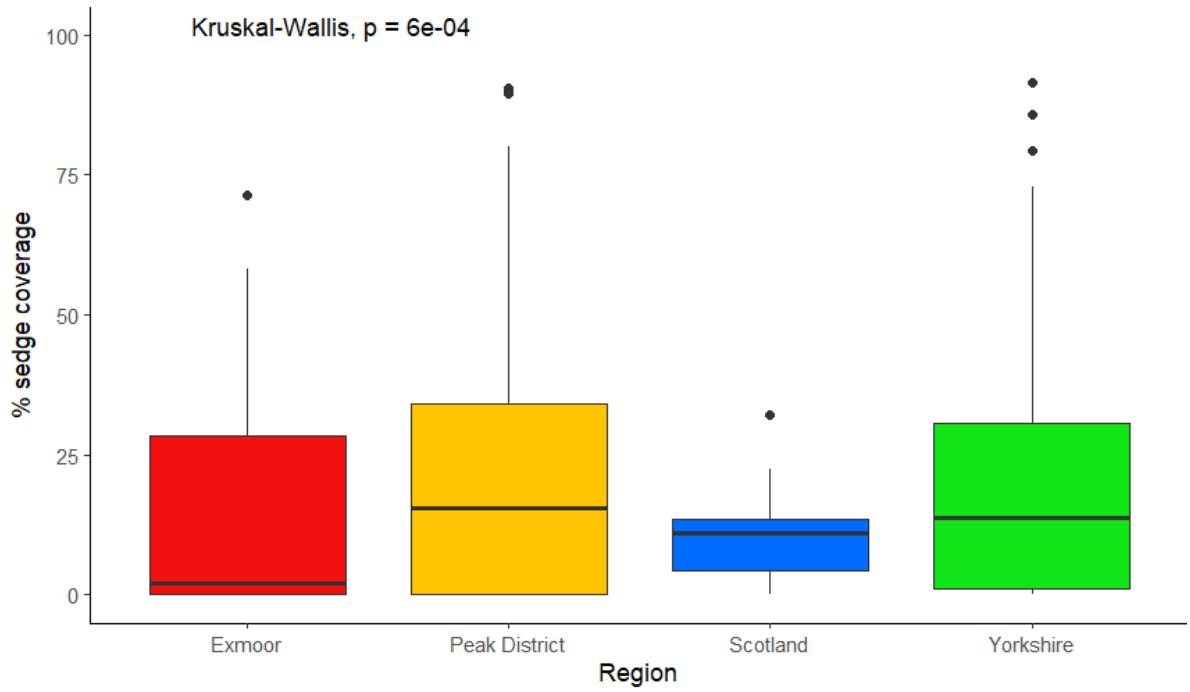


Figure 6.3 % sedge coverage of mesocosm cores from four regions of UK blanket bog. Outliers shown beyond the whiskers. Statistical significance test result shown.

NMDS analysis indicated that vegetation coverage on cores taken from Exmoor were distinctly different from those from the other regions (Figure 6.1). As discussed in Chapter 5, *Molinia* is the dominant vegetation on Exmoor cores and is not found elsewhere. Ellipsis showing grouping of the cores also indicated that some cores from The Peak District are different causing the skew in NMDS1. These cores are the degraded cores which were void of vegetation (discussed further in Chapter 5).

6.3.3 Soil parameters

Bulk density was highest in samples from Yorkshire and lowest in samples from the Peak District (median 0.1 g cm^{-3} and 0.08 g cm^{-3} respectively). There was no significant difference in bulk density between regions (KW chi-squared = 5.38, df = 3, p = 0.15; Figure 6.3 A). % C_{org} was significantly lower in samples from Exmoor compared to Yorkshire and Scotland (KW chi-squared = 9.57, df = 3, p = 0.015, post-hoc p = 0.03; Figure 6.3 B).

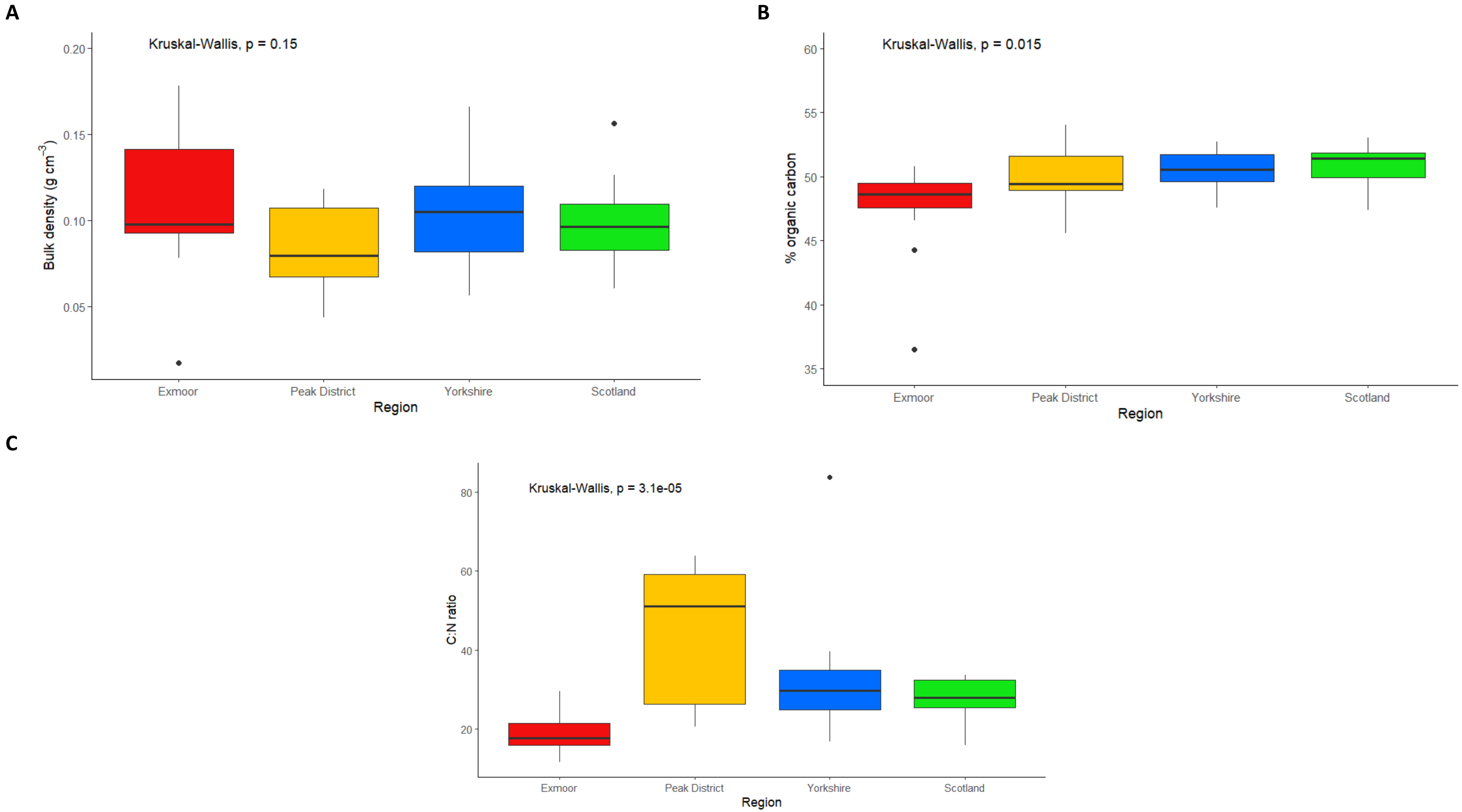


Figure 6.4 Soil properties (A = bulk density, B = % organic carbon, and C) carbon: nitrogen ratio) of peat samples collected alongside mesocosms from blanket bog from four UK climatic regions. Statistical significance testing result displayed.

A NMDS was performed to determine if climatic region had a significant impact on soil quality parameters (i.e., bulk density, % C_{org}, and C:N). Region was used to center the scores for the NMDS, and environmental parameters were used as vectors. NMDS (Figure 6.5) indicated that longitude, latitude, elevation, peat depth, and % coverage of grass and bare peat were likely significant drivers in variations of soil parameters (Table 6.4). ANOSIM analysis indicated that based on the groupings in the NMDS, soil parameters differed significantly between climatic regions (ANOSIM R = 0.27, p = 0.001).

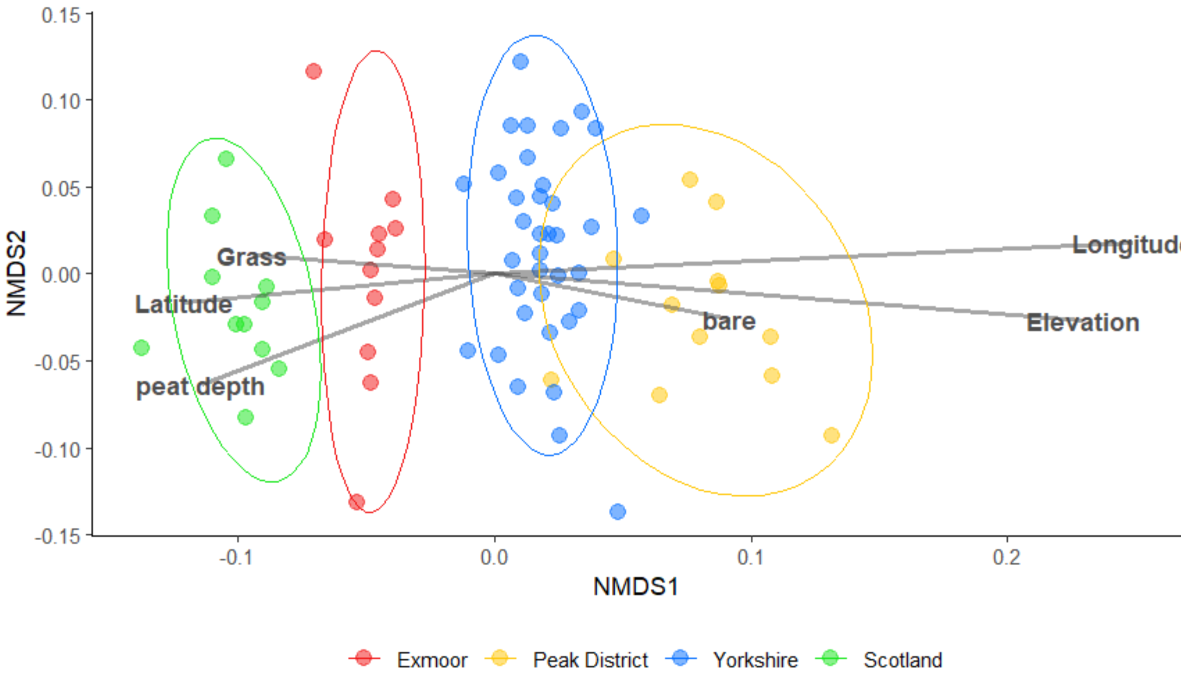


Figure 6.5 NMDS of soil parameters (bulk density, soil moisture, % organic carbon, and carbon:nitrogen ratio) of soil samples taken alongside mesocosm central cores from four regions in the UK. Ellipses show grouping of cores from the same region. Region is indicated by colour. Vegetation groups and site condition most strongly associated with regions are shown.

Table 6.4 Non-metric multidimensional scaling analysis (NMDS) R^2 and probability scores for vectors used in NMDS analysis for the factors relating to soil quality parameters (bulk density, soil moisture, % C_{org}, and C:N). Parameters with significant p values are indicated in **bold**.

	NMDS 1	NMDS 2	R^2	Pr (>r)
Latitude	**-0.99**	**-0.13**	**0.19**	**0.002**
Longitude	**0.99**	**0.07**	**0.81**	**0.001**
Slope	**0.82**	**0.58**	**0.13**	**0.01**
Aspect	-0.30	-0.96	0.02	0.59
Elevation	**0.99**	**-0.11**	**0.70**	**0.001**
Peat Depth	**-0.87**	**-0.49**	**0.22**	**0.001**
% C. vulgaris	0.63	0.78	0.04	0.31
% Moss	-0.64	-0.76	0.01	0.72
% Sedge	0.99	-0.13	0.006	0.81
% Shrub	0.61	-0.79	0.04	0.27
% Grass	**-0.99**	**0.12**	**0.11**	**0.013**
% Bare	**0.96**	**-0.27**	**0.12**	**0.016**

6.3.3.1 Water extractable DOC

Water extractable DOC (WEDOC) was extracted from each of the soil samples collected alongside the mesocosm cores and analysed for DOC concentration and UV_{abs} at key wavelengths. WEDOC ranged from 9.2 mg L^{-1} to 40.4 mg L^{-1} with a median of 19.2 mg L^{-1} and a mean of 20.6 ± 7.4 mg L^{-1}. WEDOC concentration was significantly lower in the Peak District samples compared to all other sites. Concentration in samples from Yorkshire were significantly lower compared to samples from Exmoor and Scotland (KW chi-squared = 29.29, df = 3, p < 0.01, post-hoc p < 0.001; Figure 6.6). There was however no significant difference in UV_{254} absorbance between regions (KW chi-squared = 6.9, df = 3, p = 0.07). Whilst samples from the Peak District had the lowest median WEDOC concentration, they had the highest median UV_{254} absorbance. $SUVA_{254}$ differed significantly between regions, but this likely reflects the differences in DOC concentration.

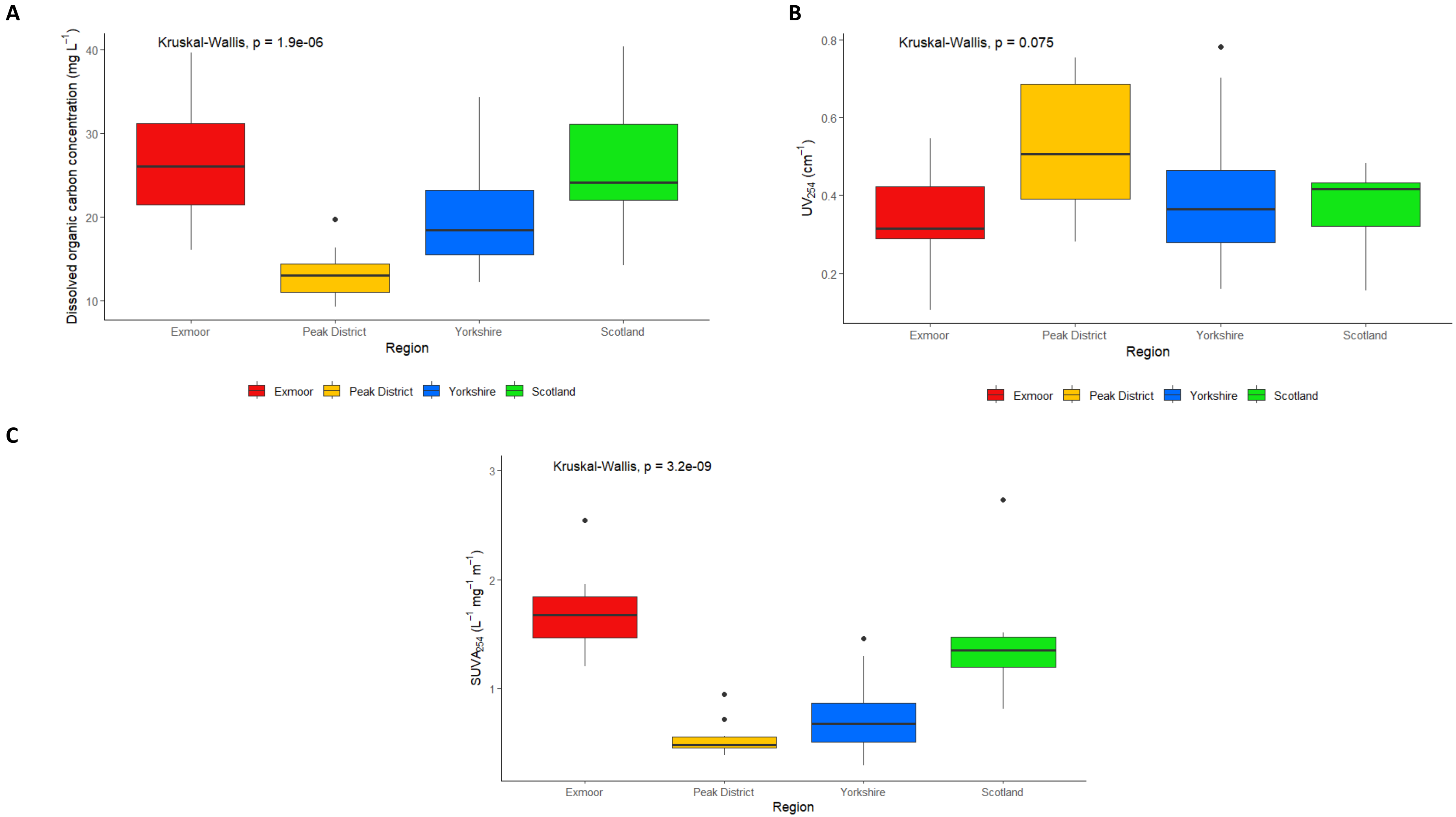
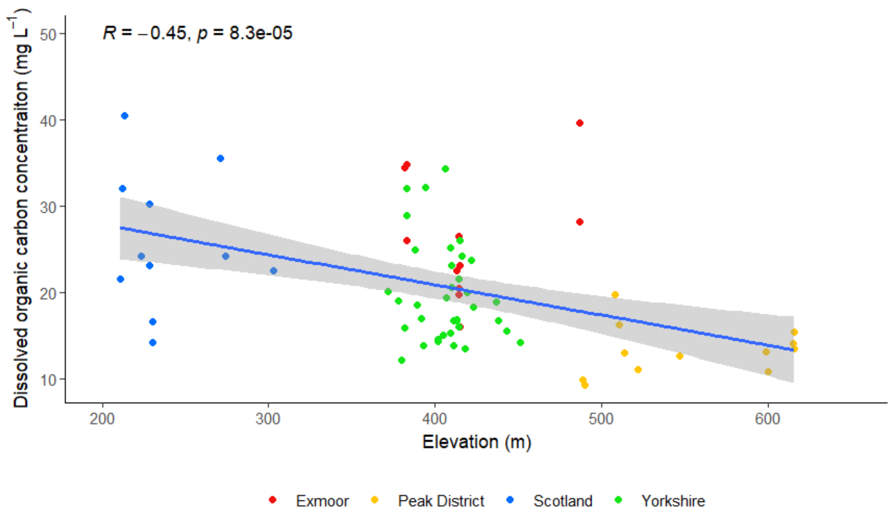


Figure 6.6 Results of analysis of peat soil samples following manual stomaching. Water extractable dissolved organic carbon concentration (A), UV_{254} absorbance (B), and $SUVA_{254}$ (C) from peat samples collected alongside mesocosm cores approx. -5 cm to – 15 cm below the peat surface for four UK blanket bog regions. Statistical significance test result shown. Outlier shown beyond the whisker.

Lower WEDOC was significantly associated with more westerly longitudes R = -0.53, $p < 0.01$; Figure 6.6 A), elevation (R = -0.45, $p < 0.01$; Figure 6.6 B), and % bare ground coverage (R = -0.24, p = 0.04; Figure 6.7 C). UV_{254} was significantly positively correlated with longitude (R = 0.29, p = 0.01) and elevation (R = 0.33, p = 0.004).

A



B

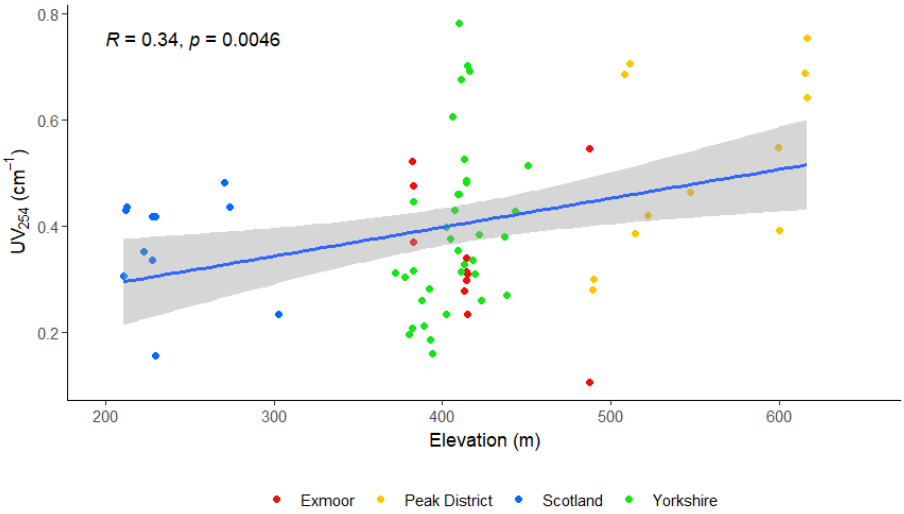


Figure 6.7 Correlations between **A)** Elevation and water extractable dissolved organic concentration and **B)** elevation and UV_{254} absorbance for soil samples from blanket bog in 4 different climatic regions in the UK. Correlation coefficient (Pearson) and R value shown.

6.3.4 Water quality

The following sections describe results from the analysis of mesocosm porewater samples which were collected on a seasonal basis.

A NMDS was performed on all water quality variables (stress = 0.14; Figure 6.7; Table 6.5) and demonstrated that WQ differed between regions (ANOSIM, R stat = 0.18, RMSE < 0.01). Exmoor is pulled by both NMDS1 and NMDS2 and differed in its DOC concentration and UV absorbance in comparison to other regions (Sections 6.4.3.1 and 6.3.4.2). In comparison to the NMDS performed on vegetation coverage, water quality from the Peak District cores were not separated from the other regions suggesting that the absence of vegetation on degraded cores did not have a significant effect of WQ parameters. Exmoor cores were separated due to *Molinia* coverage in Figure 6.1 and were also separated when considering WQ parameters. ANOSIM analysis indicated that water quality significantly differed between region (ANOSIM statistic = 0.18, p < 0.001).

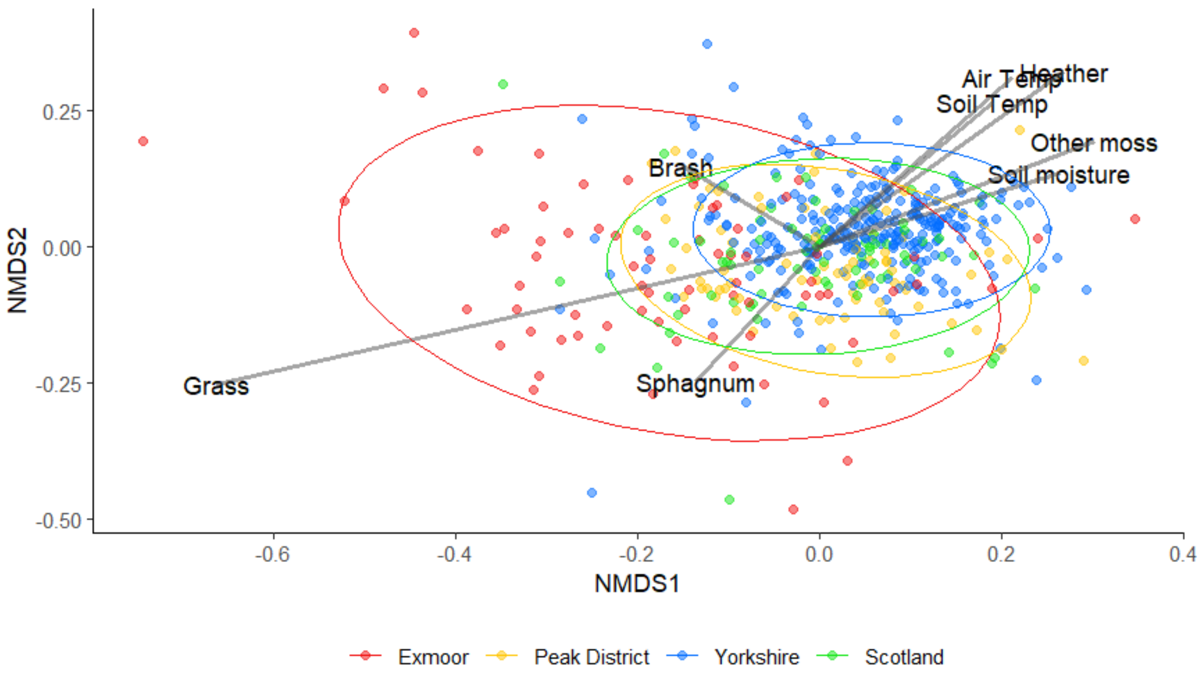


Figure 6.8 NMDS on water quality variables (DOC, TbN, pH, conductivity, and UV absorbance at key wavelengths) on mesocosm porewater samples from blanket bogs in four UK climatic regions. Ellipsis show groupings of site data. Significant variables in driving differences in water quality are shown.

Table 6.5 Non-metric dimensional scaling analysis on water quality variables (DOC, DON, pH, conductivity, and UV absorbance at key wavelengths) on mesocosm porewater samples from blanket bog in four UK climatic regions. Likely significant variables shown in **bold.**

	NMDS 1	NMDS 2	R^2	Pr (>r)
Air temperature	**0.56**	**0.82**	**0.07**	**0.001**
Soil temperature	**0.58**	**0.81**	**0.06**	**0.001**
Soil moisture	**0.89**	**0.50**	**0.04**	**0.001**
Light	-0.62	0.79	0.009	0.09
% C.vulgaris	**0.64**	**0.77**	**0.09**	**0.001**
% shrub	0.77	0.63	0.02	0.008
% herb	-0.91	-0.42	0.007	0.19
% sedge	0.37	-0.93	0.003	0.53
% *Sphagnum*	**-0.48**	**-0.88**	**0.04**	**0.002**
% Other moss	**0.84**	**0.54**	**0.06**	**0.001**
% Grass	**-0.93**	**-0.36**	**0.26**	**0.001**
% Lichen	0.27	-0.96	0.0002	0.95
% Bare	0.68	-0.73	0.01	0.091
% Brash	**0.45**	**-0.89**	**0.02**	**0.007**
% pel_lac	0.45	-0.89	0.009	0.098
% Luzula	-0.11	0.99	0.0027	0.38
% Salez	-0.61	-0.79	0.006	0.16

6.3.4.1 Dissolved organic carbon

DOC concentrations ranged from 2.9 – 397.9 mg L^{-1} with a mean of 64.4 ± 43.5 mg L^{-1}. Concentrations differed significantly between all regions (excluding Scotland-the Peak District; KW chi-squared = 173.78, df = 3, $p < 0.01$; post-hoc $p < 0.01$) with samples from Exmoor cores having the lowest median concentration whilst samples from Yorkshire cores had the highest (72.8 mg L^{-1} and 25 mg L^{-1} respectively; Figure 6.9).

Median DON concentration showed similar trends to DOC and was highest in Yorkshire cores (3 mg L^{-1}) and lowest in Exmoor cores (1.2 mg L^{-1}). DON concentration was significantly correlated with DOC (R = 0.61, $p < 0.01$, method = Pearson; Figure 6.10) and differed significantly between site (KW chi-squared = 99.66, df = 3, $p < 0.01$).

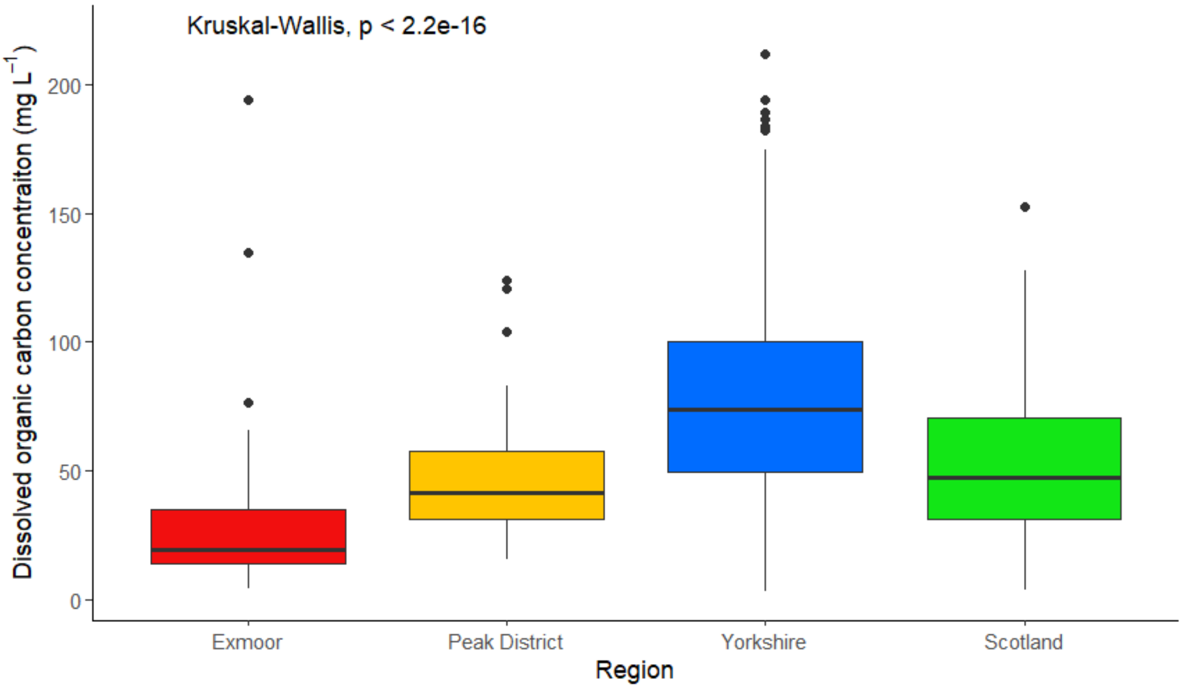


Figure 6.9 Dissolved organic carbon concentration of mesocosm porewaters from four UK climatic regions. Yorkshire comprises of three grouse-managed blanket bog. Significance test result shown.

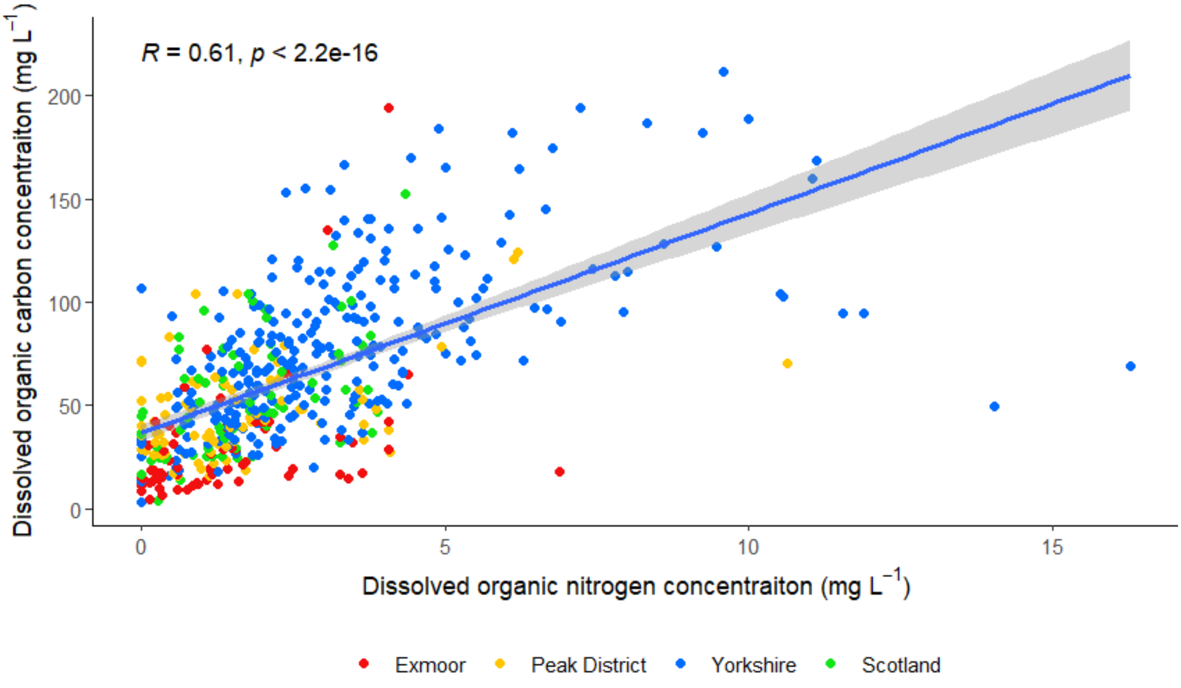


Figure 6.10 Correlation between mesocosm porewater dissolved organic nitrogen concentration and dissolved organic carbon concentration. Pearson correlation analysis result shown.

GLM modelling was undertaken to determine significant drivers of DOC concentration in all sampled porewaters. Environmental variables (weather data, site data, and vegetation coverage) were centered and Z-scored prior to plotting a correlation matrix using the R package "corrplot" (Wei and Simko, 2017). The variables significantly correlated to DOC concentration are listed in Table 6.6.

Table 6.6 Environmental variables significantly correlated with mesocosm pore water dissolved organic carbon concentration in cores taken from four regions of UK blanket bog. Correlation method = Pearson.

Correlated environmental variables	R value	P value
Soil moisture (%)	0.21	< 0.001
Air temperature (°C)	0.27	< 0.001
pH	-0.22	< 0.001
Conductivity	0.29	< 0.001
% *Calluna vulgaris* coverage	0.25	< 0.001
% *Sphagnum* spp. coverage	-0.19	< 0.001
% grass coverage	-0.33	< 0.001
% other moss coverage	0.25	< 0.001
Dissolved organic nitrogen (mg L^{-1})	0.61	< 0.001

Relationships between DOC concentration and environmental variables (Table 6.6) were assessed using a GLM as DOC concentration was approaching a normal distribution and was continuous and unbounded. To address issues of multi-collinearity, variables (soil moisture, pH, conductivity) were removed from the dataset. Latitude and longitude of core collection sites were removed as they were no longer a representation of the climatic conditions which the peat cores were under. Multi-collinearity was assessed though variance inflation factors (VIF) using the "car" R package (Fox & Weisberg, 2019). The initial model run showed VIF values < 2 for all variables. A model was obtained using 6 variables: air temperature, % *C. vulgaris* cover, % grass cover, % *Sphagnum* spp. cover, and % other moss cover, DON concentration (Table 6.7).

Table 6.7 Estimates, error, T, P, VIF (variance inflation value) and AIC values of a general linear model assessing the significance of environmental variables on DOC concentration. Significant variables shown in bold.

Coefficients	Estimate	Std. Error	T value	*p*-value	VIF	AIC
Intercept	**21.36**	**4.59**	**4.65**	**< 0.001**		4699.7
% C. vulgaris cover	**0.16**	**0.08**	**2.08**	**0.04**	1.18	
% *Sphagnum. spp* cover	**-0.14**	**0.07**	**-2.08**	**< 0.001**	1.28	
% grass cover	**-0.46**	**0.09**	**-5.26**	**0.04**	1.25	
% other moss cover	0.07	0.07	1.06	0.29	1.31	
Dissolved organic nitrogen	**8.86**	**0.61**	**14.43**	**< 0.001**	**1.13**	
Air temperature	**1.76**	**0.31**	**5.75**	**< 0.001**	**1.02**	

% *Sphagnum* coverage was identified as a significant driver of DOC concentration and was significantly negatively correlated (Table 6.6). % grass coverage was also a significant driver of, and significantly negatively correlated with DOC concentration albeit less strongly. % *C. vulgaris* coverage and air temperature were significantly positively correlated and were identified as significant drivers of DOC concentration.

6.3.4.2 UV absorbance

6.3.4.2.1 UV_{254} and $SUVA_{254}$

UV_{254} absorbance ranged from 0.056 – 5.45 cm^{-1} with a mean of 2.6 ± 1.4 cm^{-1} and a median of 2.54 cm^{-1}. UV_{254} absorbance differed significantly between all regions (KW chi-squared = 119.76, df = 3, $p < 0.01$, pairwise Wilcoxon $p < 0.01$; Figure 6.11) excluding Scotland and the Peak District. Median UV_{254} absorbance was highest in porewaters from Yorkshire cores (2.26 cm^{-1}) and lowest in cores from Exmoor (0.96 cm^{-1}). $SUVA_{254}$ was shown to differ significantly between regions (KW chi-squared = 11.55, df = 3, $p = 0.009$; Figure 6.12) however post-hoc testing indicated that only Exmoor differed significantly from other sites ($p < 0.05$). Exmoor had the lowest mean $SUVA_{254}$ of 4.4 ± 3.7 L^{-1} mg^{-1} m^{-1} whilst the Peak District had the highest mean of 5.4 ± 3 L^{-1} mg^{-1} m^{-1}. $SUVA_{400}$ was significantly lower in Exmoor cores compared to the other regions (KW chi-squared = 36.63, df = 3, $p < 0.01$, median 0.39 L^{-1} mg^{-1} m^{-1}, 0.67 L^{-1} mg^{-1} m^{-1}, 0.62 L^{-1} mg^{-1} m^{-1}, and 0.62 L^{-1} mg^{-1} m^{-1} for Exmoor, the Peak District, Yorkshire, and Scotland respectively).

UV_{254} and UV_{400} was significantly correlated with DOC concentration for all and each individual region/s (Table 6.8). UV_{400} showed higher correlation coefficients for each region and was highest for Exmoor cores.

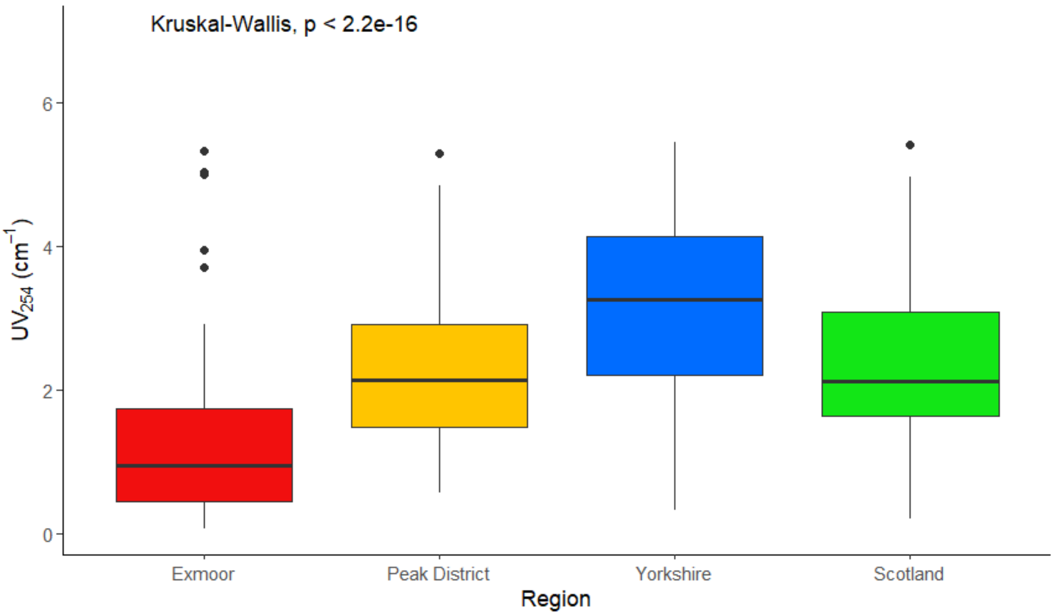


Figure 6.11 UV_{254} of mesocosm porewater samples from blanket bog from four climatic regions in the UK. Yorkshire comprises of three grouse-managed blanket bog sites. Outliers shown beyond the whiskers. Significance testing result shown.

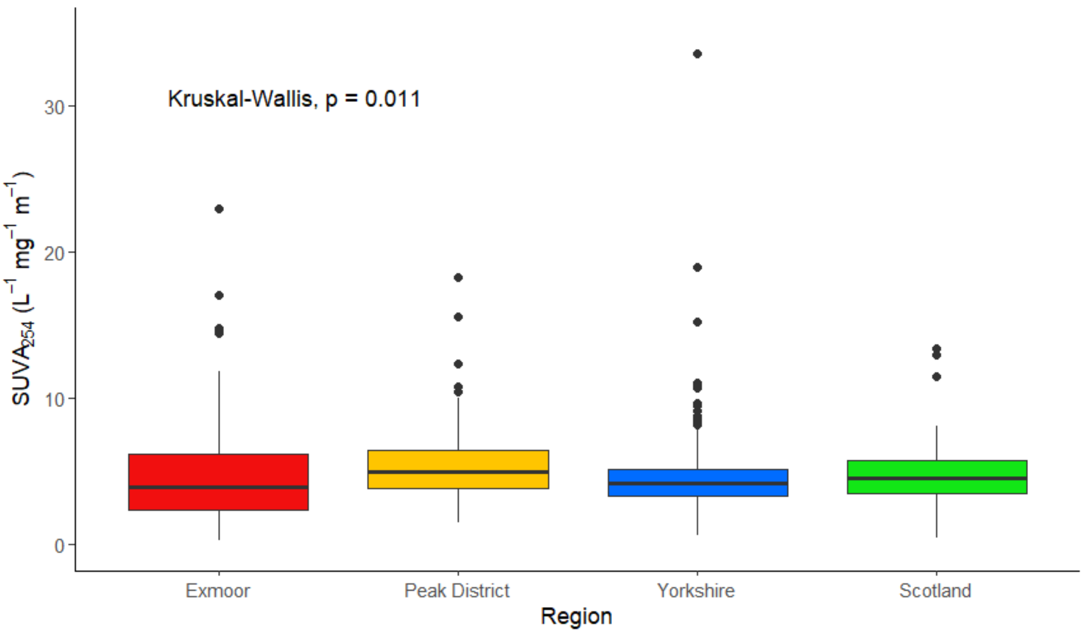


Figure 6.12 $SUVA_{254}$ of mesocosm porewater samples from blanket bog from four climatic regions in the UK. Yorkshire comprises of three grouse-managed blanket bog sites. Outliers shown beyond the whiskers. Significance testing result shown.

Table 6.8 Correlation coefficient (method = Pearson) and p values for UV_{254} and UV_{400} absorbance and dissolved organic carbon concentration for mesocosm porewaters from four regions of UK blanket bog.

	UV_{254}		UV_{400}	
	R	p	R	p
All regions	0.69	< 0.01	0.71	< 0.01
Exmoor	0.69	< 0.01	0.82	< 0.01
Peak District	0.51	< 0.01	0.51	< 0.01
Yorkshire	0.54	< 0.01	0.61	< 0.01
Scotland	0.58	< 0.01	0.59	< 0.01

6.3.4.2.2 Hazen

Hazen ranged from 3.6 to 1752 with a median of 330. Hazen was significantly lower in Exmoor samples compared to the other regions (KW chi-squared = 94.53, df = 3, $p < 0.01$; Figure 6.12). Median hazen of Exmoor samples was 126 compared to 357.6, 372, and 367.9 for samples from the Peak District, Yorkshire, and Scotland respectively.

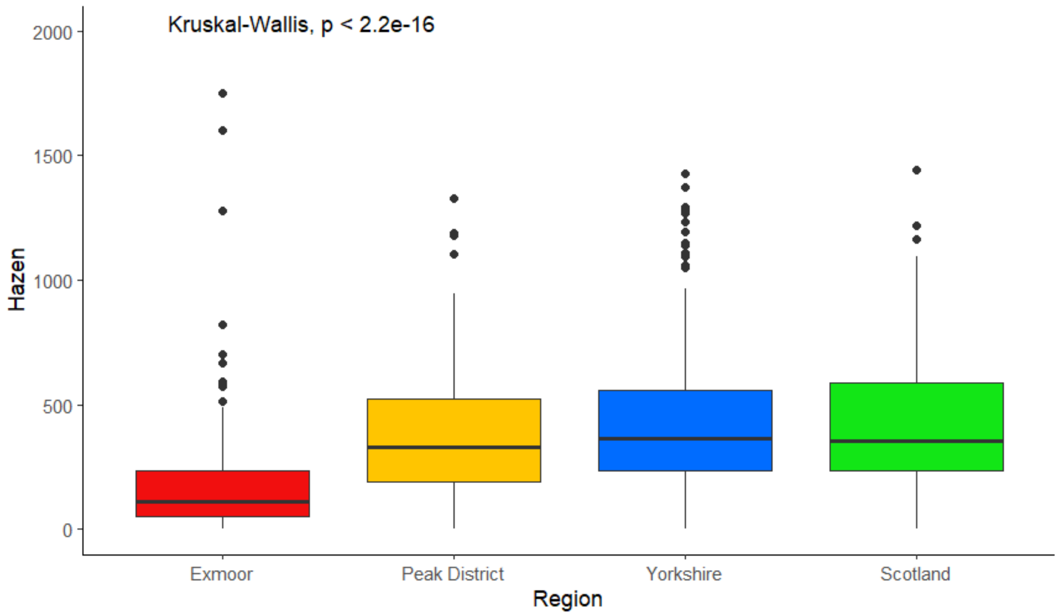


Figure 6.13 Hazen of mesocosm porewater samples from blanket bog from four climatic regions in the UK. Yorkshire comprises of three grouse-managed blanket bog sites. Outliers shown beyond the whiskers. Significance testing result shown.

6.3.4.3 pH

618 samples were analysed for pH. pH ranged from 3.24 – 5.55 with a median of 4.14 and a mean of 4.19 ± 0.37. pH differed significantly between regions (KW chi-squared = 173.82, df = 3, $p < 0.01$; Figure 6.14). pH of Exmoor and Scotland porewaters was significantly higher than those from the other regions (post-hoc $p < 0.01$). pH was significantly negatively correlated with DOC concentration (R = - 0.22, $p < 0.001$, method = Pearson) and UV_{254} absorbance (R = -0.27, $p < 0.001$). % grass coverage and pH were positively correlated (Table 6.9).

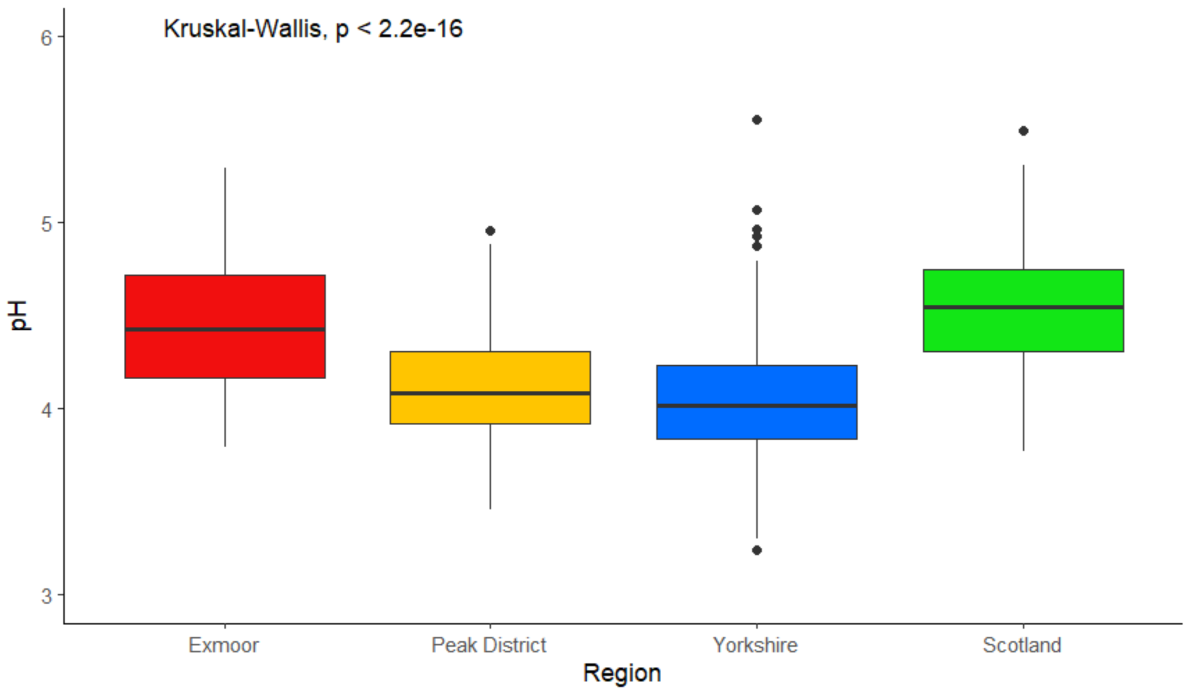


Figure 6.14 pH of mesocosm porewaters from four regions of UK blanket bog. Statistical significance test result shown. Outliers shown beyond the whisker.

Table 6.9 Correlation coefficient and significance values for pH (of mesocosm porewater samples) and vegetation coverage on mesocosm cores. Correlation method = Pearson.

Vegetation type	R	p-value
Calluna vulgaris	-0.16	0.0003
Grass	0.25	< 0.001
Sphagnum spp	0.25	< 0.001
Sedge	-0.11	0.01
Other moss	-0.20	< 0.01

6.3.4.4 *Conductivity*

Mesocosm porewater conductivity ranged from 11.27 μs cm^{-1} to 381 μS cm^{-1} with a median of 82.35 μs cm^{-1}. Conductivity was significantly higher in samples from Yorkshire cores (KW chi-squared = 59.78, df = 3, $p < 0.001$, post-hoc $p < 0.001$; Figure 6.15) compared to all other regions.

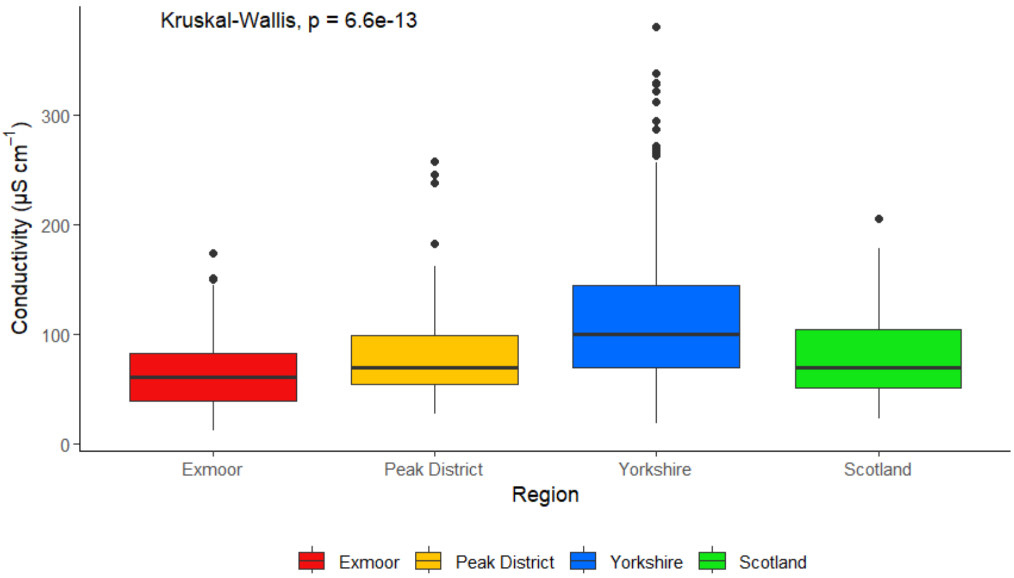


Figure 6.15 Conductivity of peat mesocosm porewaters from four regions of UK blanket bog. Yorkshire comprises of three sites. Outliers shown beyond the whisker. Significance testing result shown.

6.3.5 Gas Fluxes

Gas flux measurements consisted of soil respiration (SR), net ecosystem exchange (NEE), ecosystem respiration (R_{eco}), and methane flux. Collection dates are listed in Table 3.19.

6.3.5.1 *Soil respiration*

SR of uncut side cores ($SR_{uncut,}$ i.e., root + microbial respiration) ranged from 0.001 to 15.1 μmol CO_2 m^{-2} s^{-1} with a median of 0.87 μmol CO_2 m^{-2} s^{-1}. As discussed in previous chapters, SR of cut cores is not considered here as the partitioning of fluxes by root cutting was not successful (shown in Chapter 4 and Chapter 5). SR_{uncut} differed significantly between region (Figure 6.16; KW chi-squared = 16.57, df = 3, $p < 0.01$) and was significantly higher in cores from Yorkshire compared to Scotland ($p < 0.01$). SR was significantly positively correlated to water table depth (R = 0.23, $p < 0.01$) and temperature (R = 0.67, $p < 0.01$), and negatively correlated with % bare peat coverage (R = -0.15, $p < 0.001$).

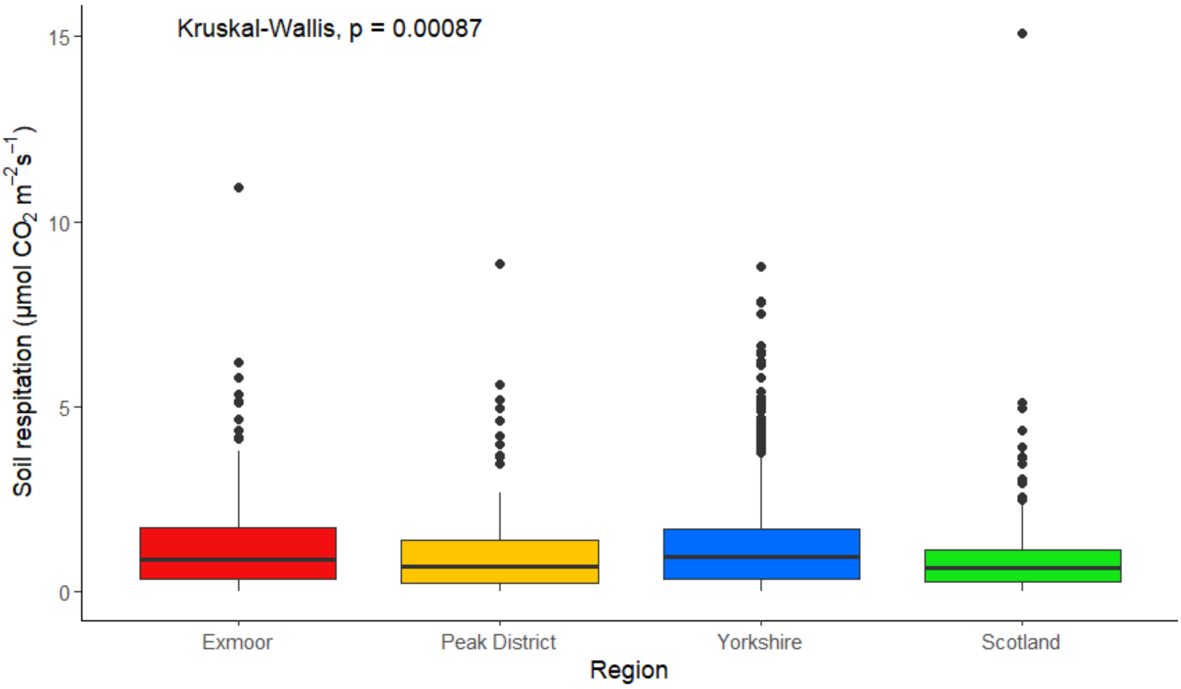


Figure 6.16 Soil respiration of side 'uncut' (i.e., roots permitted to grow) mesocosm cores from four regions of UK blanket bog. Outliers shown beyond the whiskers. Statistical significance test result shown.

6.3.5.2 Net ecosystem exchange

NEE ranged from -32.19 µmol CO_2 m^{-2} s^{-1} to -0.01 µmol CO_2 m^{-2} s^{-1} with a median of -3.19 µmol CO_2 m^{-2} s^{-1} (Table 6.10). NEE differed significantly between regions (Figure 6.17, post-hoc p values presented in Table 6.11) whereby Exmoor cores had the lowest median NEE (-4.75 µmol CO_2 m^{-2} s^{-1}) and Peak District cores had the highest (-2.492 µmol CO_2 m^{-2} s^{-1}).

Table 6.10 Descriptive statistics for net ecosystem exchange flux (µmol CO_2 m^{-2} s^{-1}) from four regions of UK blanket bog.

	Minimum	Maximum	Median
All regions	-32.19	-0.01	-3.19
Exmoor	-32.19	-0.13	-4.75
Peak District	-15.81	-0.01	-2.92
Yorkshire	-14.93	-0.01	-3.39
Scotland	-19.87	-0.11	-2.22

NEE differed significantly seasonally (KW chi-squared = 291.54, df = 3, $p < 0.001$) whereby NEE fluxes were significantly higher in winter, and fluxes were significantly lower in summer compared to all other seasons (post-hoc $p < 0.01$). There were significant differences in NEE between region on a seasonal basis (Figure 6.18). This difference was most significant in summer months where Exmoor median NEE was -17.9 2 µmol CO_2 m^{-2} s^{-1} compared to -5.6 2 µmol CO_2 m^{-2} s^{-1}, -3.5 2 µmol CO_2 m^{-2} s^{-1}, and -6.32 2 µmol CO_2 m^{-2} s^{-1} for the Peak District, Scotland, and Yorkshire respectively.

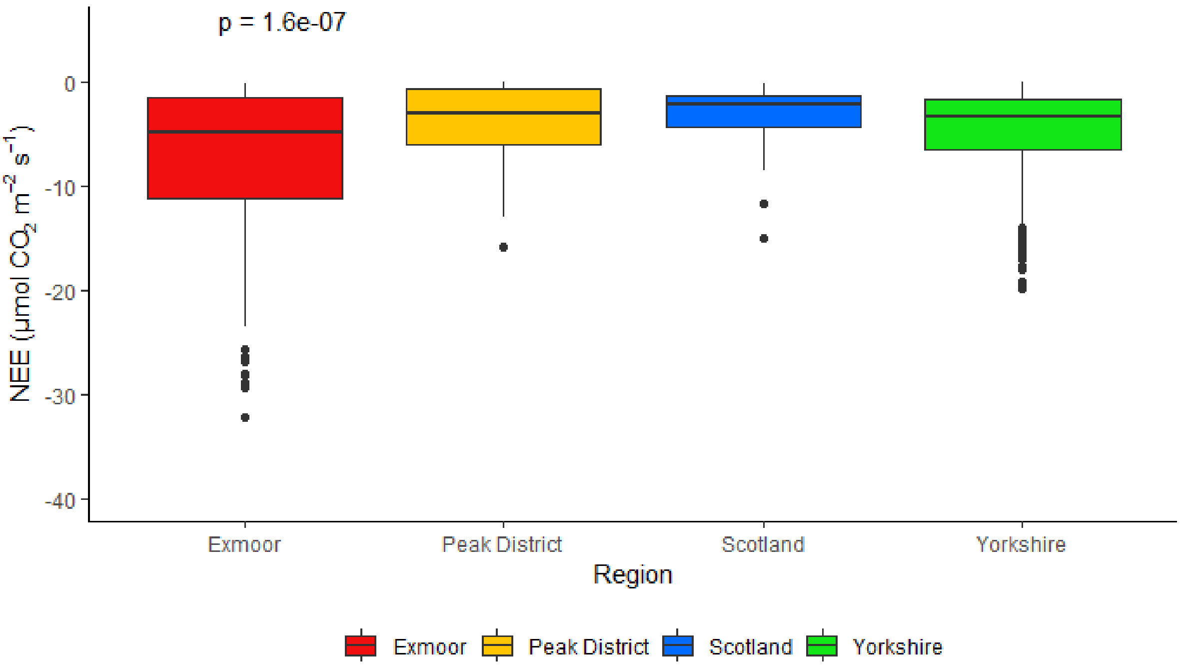


Figure 6.17 Net ecosystem exchange (NEE; µmol CO_2 m^{-2} s^{-1}) of central mesocosm cores from four regions of UK blanket bog. Statistical significance test result shown. 1 outlier removed according to statistical methodology.

Table 6.11 Post-hoc (Pairwise Wilcoxon) testing p-values for significant differences in net ecosystem exchange (NEE; µmol CO_2 m^{-2} s^{-1}) for mesocosm cores from four UK blanket bog regions. Significant differences shown in bold.

	Exmoor	Peak District	Scotland
Peak District	**0.001**	-	-
Scotland	**0.002**	0.58	-
Yorkshire	0.32	**0.001**	**0.0009**

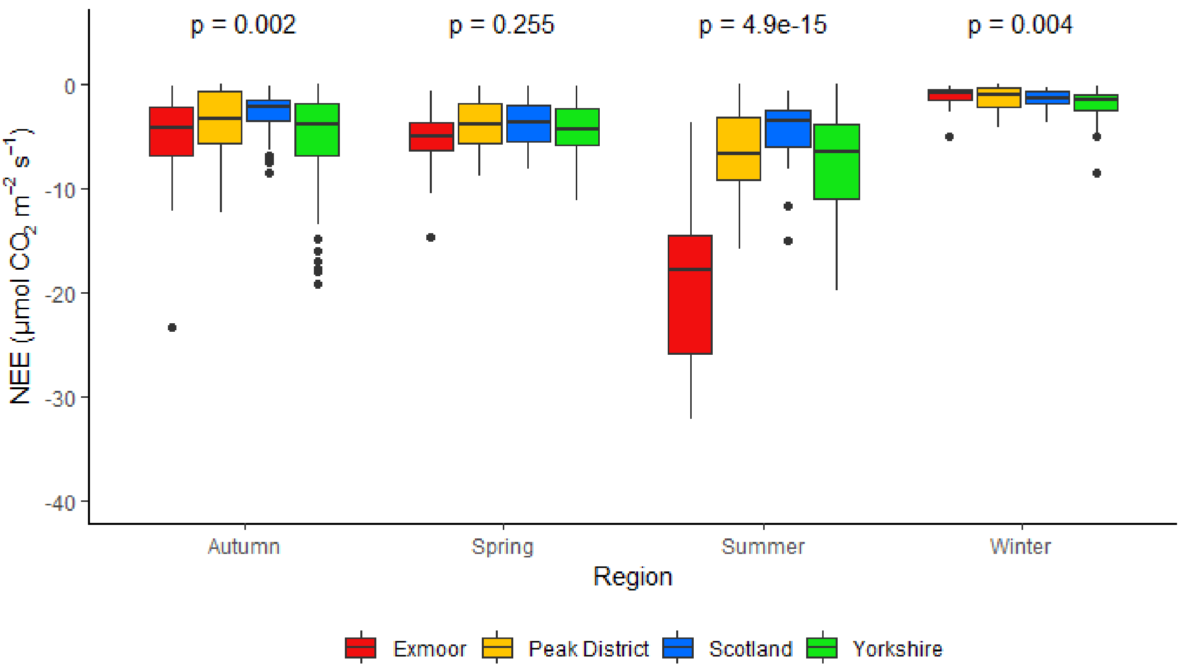


Figure 6.18 Seasonal net ecosystem exchange (NEE; µmol CO_2 m^{-2} s^{-1}) of central mesocosm cores from four regions of UK blanket bog. Statistical significance test result shown.1 outlier removed according to statistical methodology.

6.3.5.3 Ecosystem respiration

R_{eco} ranged from 0.03 µmol CO_2 m^{-2} s^{-1} to 22.19 µmol CO_2 m^{-2} s^{-1} with a median of 2.76 µmol CO_2 m^{-2} s^{-1}. Reco was significantly higher in cores from Exmoor and Yorkshire (median R_{eco} of 3.33 µmol CO_2 m^{-2} s^{-1} and 3.18 µmol CO_2 m^{-2} s^{-1} respectively) compared to the Peak District and Scotland (median R_{eco} 1.91 µmol CO_2 m^{-2} s^{-1} and 2.07 µmol CO_2 m^{-2} s^{-1}; KW chi-squared = 50.85, df = 3, $p < 0.01$; post-hoc $p < 0.01$).

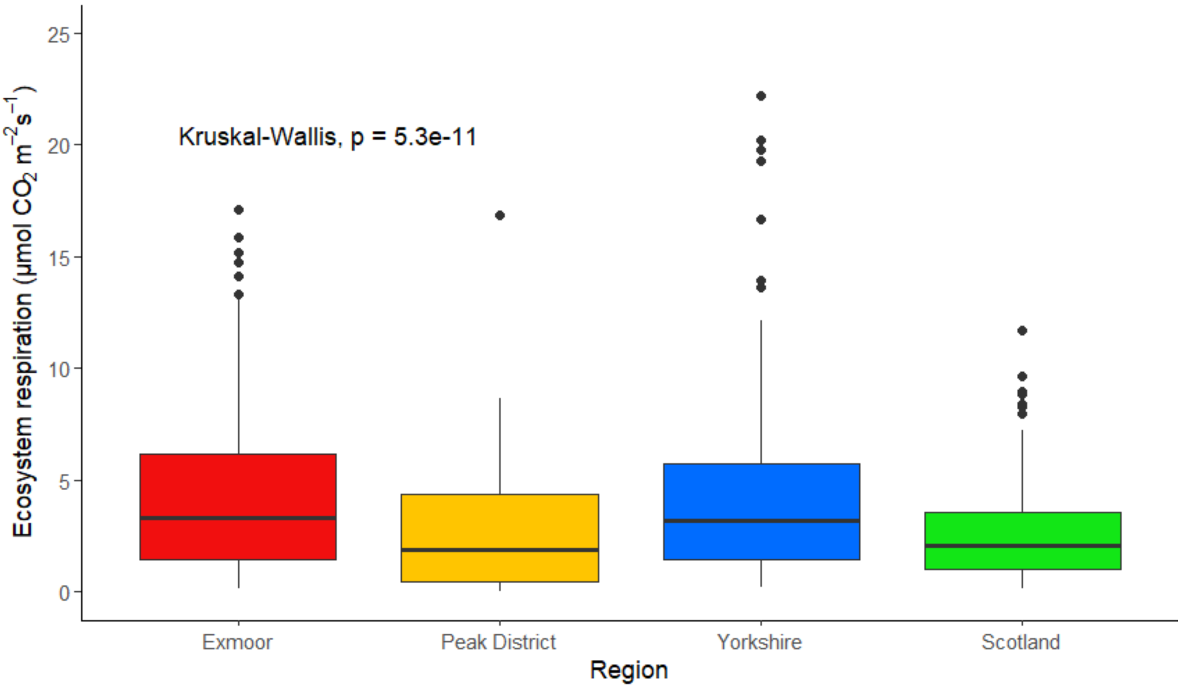


Figure 6.19 Ecosystem respiration (R_{eco}; µmol CO_2 m^{-2} s^{-1}) of central mesocosm cores from four regions of UK blanket bog. Statistical significance test result shown. 1 outlier removed according to statistical methodology.

6.3.5.4 Methane flux

9 outlier results were removed according to statistical methodology. CH_4 flux ranged from 0.001 nmol CH_4 m^{-2} s^{-1} to 5030 nmol CH_4 m^{-2} s^{-1} with a median of 12.4 nmol CH_4 m^{-2} s^{-1}. CH_4 flux differed significantly between region (KW chi-squared = 88.85, df = 3, $p < 0.01$; Figure 6.20) whereby the flux from the Peak district cores was significantly lower than all other regions ($p < 0.01$). The Peak District cores were significantly associated with % bare peat coverage (Section 6.2.2), however % bare peat only weakly correlated with CH_4 flux (R = -0.08). % brash, sedge, and grass coverage were significantly correlated with CH_4 flux (R = -0.12, $p < 0.01$, R = 0.17, $p < 0.01$, and R = =0.1, p = 0.04 respectively) albeit all with low correlation coefficients.

Table 6.12 Descriptive statistics for methane flux of mesocosm cores from four regions of UK blanket bog.

	Minimum	Maximum	Median
All regions	0.001	544.6	6.55
Exmoor	0.001	259.5	11.35
Peak District	0.001	86.5	2.62
Yorkshire	0.001	544.6	16.10
Scotland	0.001	190.9	20.36

CH_4 flux differed significantly between cores from different regions seasonally (Figure 6.21). In summer (when fluxes were highest), Yorkshire had the highest median CH_4 flux (76.61 nmol CH_4 m^{-2} s^{-1}) and the Peak District the lowest (7.17 nmol CH_4 m^{-2} s^{-1}).

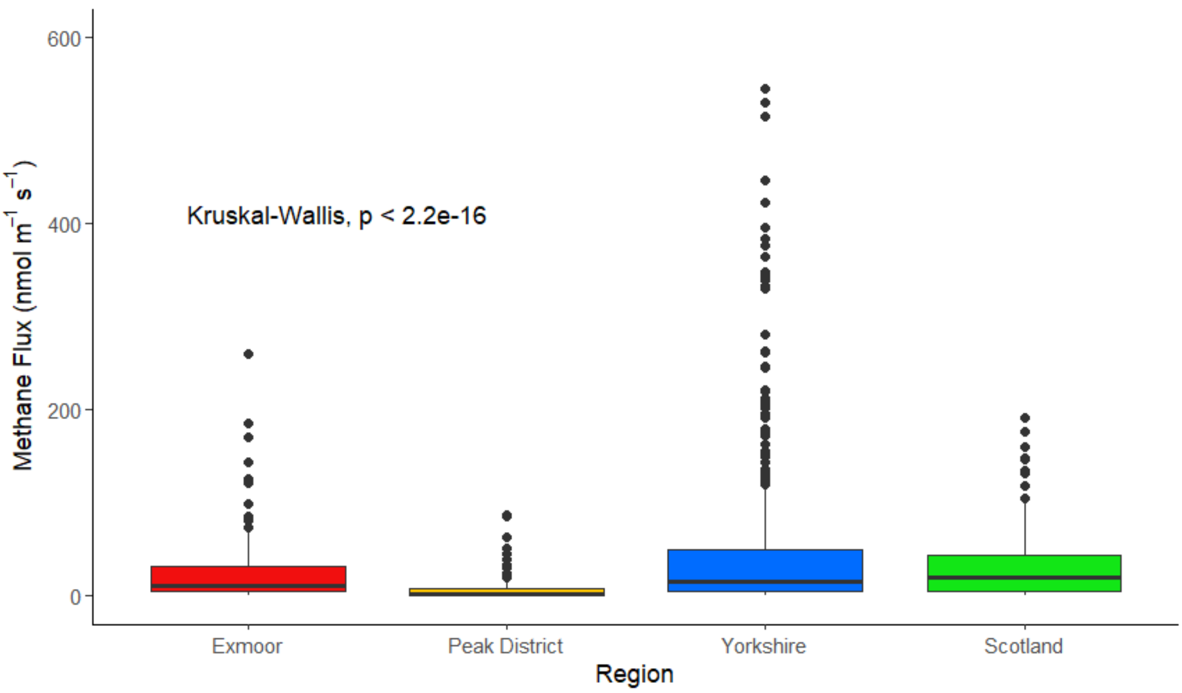


Figure 6.20 Methane flux (nmol m^{-1} s^{-1}) of mesocosm cores from four regions of UK blanket bog. 9 outliers removed according to methodology. Statistical significance test result shown.

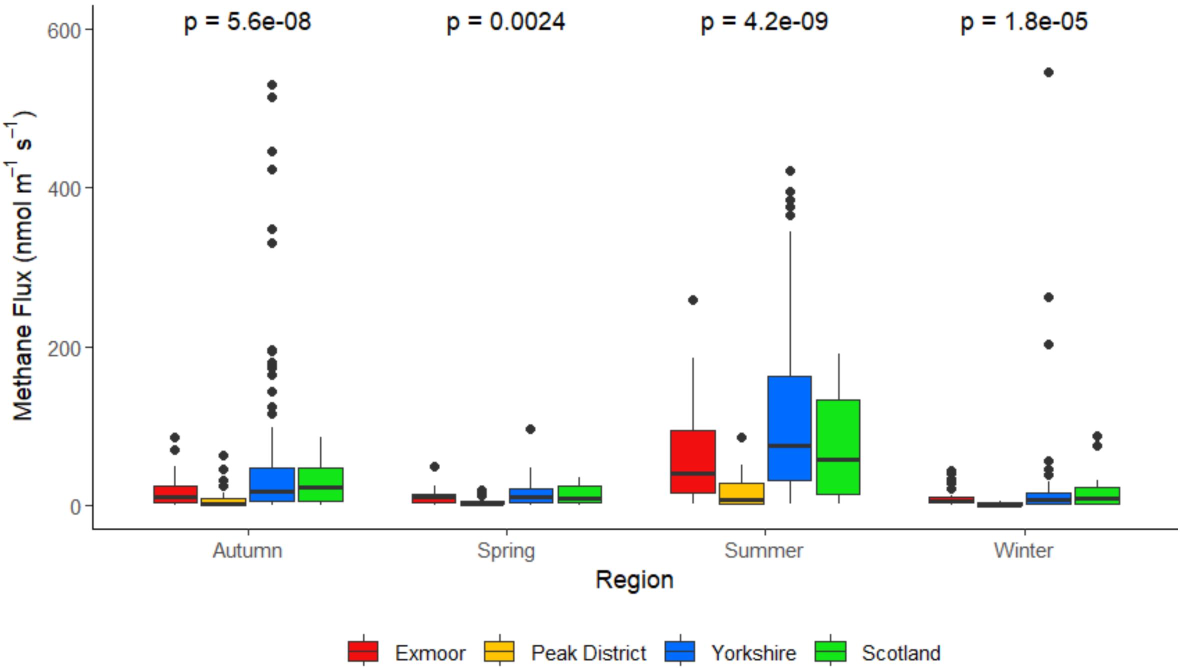


Figure 6.21 Seasonal methane flux (nmol CH_4 m^{-2} s^{-1}) of central mesocosm cores from four regions of UK blanket bog. Statistical significance test result shown.

Relationships between CH_4 flux, vegetation coverage, and environmental variables were assessed using a GLM. Latitude and longitude of core collection sites were removed as they were no longer representative of core climatic conditions. Temperature, light level, % grass, sedge, and brash coverage were significantly correlated with CH_4 flux and included in the initial model. All VIF values for the initial model were < 2 and therefore, all variables were retained. Temperature, and % brash and sedge coverage were identified as significant drivers of CH_4 flux (Table 6.11; $R = -0.11$, $p < 0.01$ and $R = 0.16$, $p < 0.01$ respectively). Temperature was most significantly positively correlated with CH_4 flux ($R = 0.28$, $p < 0.01$; Figure 6.22).

Table 6.13 Estimates, error, T, P, VIF (variance inflation value) and AIC values of a general linear model assessing the significance of environmental variables and vegetation on methane flux. Significant variables shown in bold.

Coefficients	Estimate	Std. Error	T value	*p*-value	VIF	AIC
Intercept	**-16.17**	**7.21**	**-2.24**	**0.02**		9027.5
Air temperature (°C)	**3.47**	**0.47**	**7.42**	< 0.01	1.70	
Light level (PAR)	-0.008	0.007	-1.31	0.19	1.70	
% grass coverage	-0.19	0.15	-1.31	0.19	1.15	
% brash coverage	**-0.38**	**0.17**	**-2.19**	**0.03**	**1.14**	
% sedge coverage	**0.45**	**0.11**	**4.21**	**< 0.01**	**1.10**	

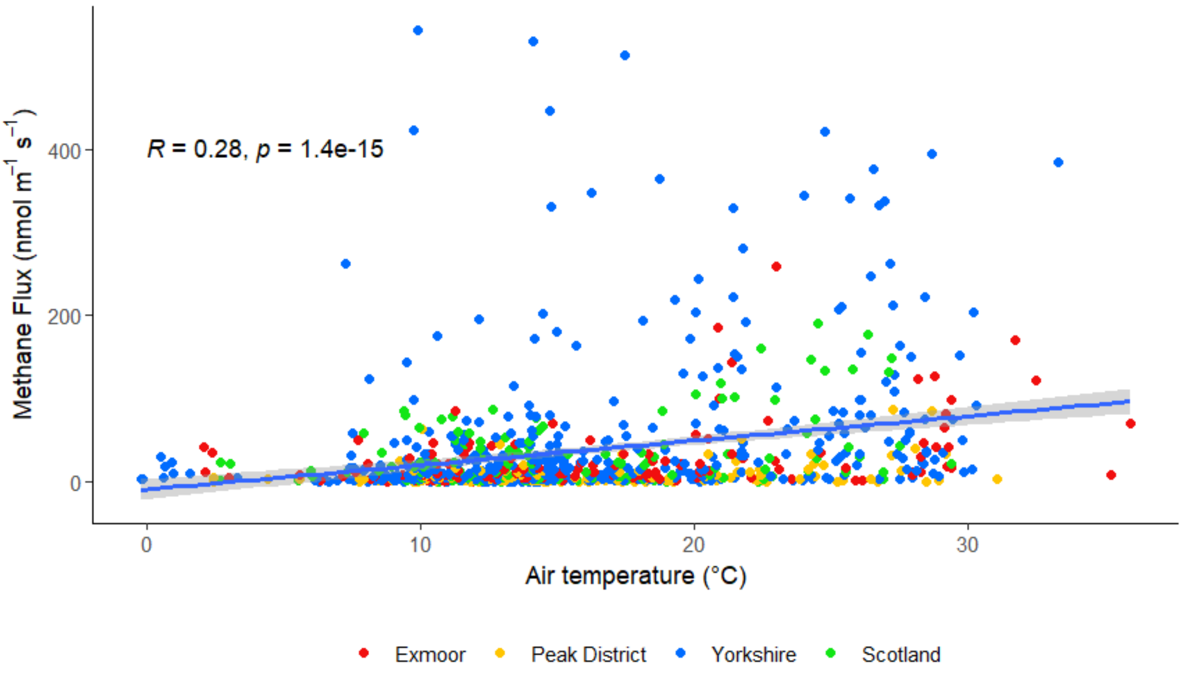


Figure 6.22 Correlation between air temperature and methane flux of mesocosm cores from four regions of UK blanket bog. Correlation coefficient shown and p value shown. 9 outliers removed according to statistical methodology.

6.3.6 Results summary

Significance test results for water quality and GHG flux between managements, sites, and within site differences as reported in this chapter are summarised in Table 6.14.

Table 6.14 Summary of p values obtained from statistical analysis of differences (Kruskal Wallis chi-squared) in key vegetation groups and water quality parameters and gas fluxes (net ecosystem exchange, ecosystem respiration, soil respiration (NEE in full light, R_{eco} in the dark, SR with roots respectively) and methane flux) between region as reported in this chapter. p values in bold indicate a significant difference (significant level $p \leq 0.05$).

	DOC	TbN	$SUVA_{254}$	Hazen	pH	% *C. vulgaris*	% *Sphagnum*	% Sedge	% Brash	% grass
Region	**$p < 0.01$**	**$p < 0.01$**	**$p < 0.01$**	**$p < 0.01$**	**$p < 0.01$**	**$p < 0.01$**	**$p < 0.001$**	**$p = 0.0005$**	**$p < 0.01$**	**$p < 0.01$**

	NEE	R_{eco}	SR	Methane
Region	**$p < 0.01$**	**$p < 0.01$**	**$p = 0.0009$**	**$p < 0.01$**

6.4 Discussion

In this work, samples, and cores from four areas of blanket bog in the UK are used to represent a climate continuum (warm-cool). This investigation is therefore considered a space-for-time (SfT) study whereby Scotland represents the past-current climate in which blanket bog is situated (cool, wet, and where a high-water table is maintained. Exmoor therefore represents the possible future climate of the areas where blanket bog is found with warmer average temperatures and lower precipitation – i.e., the limits of their bioclimatic space (Gallego-Sala *et al*., 2010) In this chapter, the effects of management and restoration which were discussed in previous chapters are not considered. Instead, results from cores of various conditions within each region are considered collectively, thereby representing blanket bog of various habitat condition found within each region.

Blanket bogs are especially vulnerable to climate change due to the narrow range of conditions required to maintain ecosystem functioning. Warmer conditions lead to increased evapotranspiration, potentially increasing the aerobic zone within the peat soil column (Salimi and Scholz, 2021), altering soil biochemical processes. In the context of restoration, there is a lot of attention on maintaining ideal peatland hydrological conditions (grip blocking to raise water table depths for example (Holden, *et al*., 2008) to prevent the decomposition of deeper, older, and more recalcitrant peat, especially as temperature sensitivity to decomposition is higher compared to more labile OM (Salimi and Scholz, 2021). It is likely that vegetation community composition will also be important in maintaining said conditions given it exerts significant control over hydrological functioning and geochemistry in blanket bog ecosystems (e.g., Heinemeyer *et al*., 2023). Mosses are expected to become less abundant whilst vascular plant cover is likely to increase with phenophases starting sooner (Antala *et al*., 2022). Changes to vegetation community composition in this way is likely to alter C assimilation and increase GHG release (higher respiration rates) (Antala *et al*., 2022).

PERMANOVA analysis indicated that temperature and precipitation (along with management and restoration status) were significant drivers of vegetation community differences between regions. Exmoor (the wettest and warmest region) was dominated by *Molinia* grass, but some cores also had significant *Sphagnum* coverage (Figure 6.2). The encroachment of vascular plants – such as *Molinia*- is a risk to intact and restored blanket bog in the context of climate change and increased anthropogenic pressures (Berendse *et al*., 2001; Voigt *et al*., 2024). However, understanding of how vascular species will affect blanket bog C fluxes and water quality is currently limited (Voigt *et al*., 2024). Water table depth has been shown to be a significant factor in the colonisation of vascular plants on blanket bog (Zarzycki *et al*., 2022) which under climate change is expected to lead to deeper water tables on blanket bog due to altered precipitation rates and higher temperatures

(Zhong *et al*., 2020). When nutrient concentrations are elevated (due to the mismanagement of land or pollution), *Molinia* out-completes peatland species as it is better adapted to higher soil nutrient concentrations (Aerts *et al*., 1992). However, in this study, porewaters from Exmoor had the lowest DON concentrations of all regions (Section 6.3.4.1). Comparative to typical upland species, their rooting systems are more extensive, facilitating colonisation of areas with fluctuating water tables.

Indicator species analysis showed that grass was significantly associated with Exmoor cores. % grass coverage was identified as a likely significant driver of DOC concentration by GLM modelling (Table 6.7), with increased coverage leading to lower DOC concentrations. However, median WEDOC concentration was highest in samples from Exmoor and UV_{254} absorbance was the lowest of all regions. Hydrophilic compounds more readily dissolve into soil porewater, and thus these results suggest that a larger portion of DOC and the peat matrix is composed of hydrophilic compounds compared to the other regions. Whilst this may be considered positive from a water treatment perspective as this DOC is more likely to be mineralised prior to reaching the water treatment works (Ritson *et al*., 2016). However, if it is not removed, it represents a significant source of DBP precursors as it is not amenable to coagulation (Sadrnourmohamadi and Gorczyca, 2015). A study by Ritson *et al* (2016) reported that WEDOC concentrations were higher from *Molinia* sources compared to *Sphagnum* and *C. vulgaris*, and WEDOC from *Molinia* sources. UV_{254} absorbance however was highest in samples from the Peak District and lowest in Exmoor samples, again indicating a more dominant hydrophilic DOC fraction in Exmoor samples. Exmoor cores also had the highest R_{eco}, due to a higher rate of decomposition compared to cores from other regions, indicating a high turnover of more labile OM.

6.4.1 Soil parameters

Median % C_{org} was significantly higher in Scotland peat soil compared to Exmoor (Figure 6.4). A higher %C_{org} suggests a lower rate of decomposition which occurs in cooler, saturated soil conditions (Conant *et al*., 2011). Exmoor soil samples had the lowest median % C_{org} which is likely due to a high *Molinia* coverage and associated deeper water tables Figure 6.3 B. Exmoor soil samples also had the lowest C:N ratio which suggests a higher rate of decomposition and C loss (Watmough *et al*., 2022), also shown by higher R_{eco} fluxes (Figure 6.19).

6.4.2 Water quality

NMDS analysis identified key vegetation groups and environmental conditions which were significant drivers of water quality parameters (DOC, UV_{abs}, pH, and conductivity; Figure 6.8). Air and soil temperature along with soil moisture were significant drivers which was expected given significant seasonal differences in DOC concentration and UV_{abs}. Vegetation coverage in Exmoor cores was a significant predicted driver of differences in water quality, indicated by the skew along both NMDS1 and NMDS2. Correlation analysis (Figure 6.10) showed that DOC in Exmoor cores did not increase as per the other regions with increased DON which is likely due to the rapid turnover of organic matter (OM) due to *Molinia* (Meade, 2015). Alongside grass coverage, *Sphagnum* coverage was significantly negatively correlated with DOC concentration (and identified as a significant driver of DOC concentration in GLM modelling; Table 6.6). Whilst *Molinia* leads to increased decomposition, *Sphagnum* inhibits decomposition and OM turnover through the production of the inhibitory compound (*Sphagnum* acid) and acidic conditions. This slowed turnover of OM leads to lower DOC production, improving water quality. Cores with higher *Sphagnum* coverage were associated with more negative NEE fluxes and is therefore beneficial for both improving water quality, and a reduction in GHG fluxes.

Due to climate change, blanket bog conditions may become less suitable for *Sphagnum* species due to increased temperatures and reduced precipitation. Periods of drought may become more frequent and degraded peatlands have been shown to be less resilient to climate change (IPCC, 2007). Currently, drought affects the treatability of DOC is not well understood although some studies have noted an increase in the hydrophilic fraction of DOC during droughts, and in the hydrophobic fraction following a drought (Clark *et al*., 2012a; Watts *et al*., 2001). Increasing *Sphagnum* coverage will be important in maintaining acidic, saturated soil environments whereby the decomposition of OM is impeded, and thus keeping blanket bogs as C sinks rather than them transitioning to C sources.

Water colour differed significantly between regions (Figure 6.11 and 6.13) with Yorkshire sites having the highest UV_{254} absorbance whilst Exmoor which had the lowest. There were no significant differences between Scotland and the Peak District samples. Yorkshire cores were significantly associated with *C. vulgaris* which has been associated with higher DOC concentrations and colour in other studies (Armstrong *et al*., 2012). Exmoor likely had the lowest median UV_{254} absorbance due to a lower DOC concentration and the rapid turnover of OM as previously discussed. Median $SUVA_{254}$ was highest in samples from the Peak District and was significantly higher compared to Exmoor samples, indicating a larger hydrophobic DOC component. As shown in Chapter 5, cores dominated by grass had the lowest $SUVA_{254}$ attributed to higher OM turnover (Figure 5.14). UV_{254} and UV_{400} were significantly correlated with DOC concentration in samples from all regions (Table 6.8) demonstrating that a significant portion of DOC from each region is composed of more recalcitrant, hydrophobic DOC. Exmoor samples showed the highest correlation coefficient for UV_{400}, which was interesting considering porewater $SUVA_{400}$ was lowest indicating that a more significant portion of DOC may be composed of more labile, non-absorbing hydrophilic compounds.

6.4.3 Gas fluxes

Changes in C cycling in northern ecosystems due to climate warming have been observed (Bubier *et al.*, 1998). GHG fluxes are reported to be higher when temperature is higher across the literature. For SR and R_{eco}, this means a greater rate of respiration, and higher C release whilst for GPP, this means a greater C uptake via photosynthesis. In blanket bog ecosystems, in addition to increased temperatures, climate warming is likely to also lead to water table drawdown which has been suggested will enhance decomposition, shifting the GHG flux balance to a net C source (Bubier *et al.*, 1998; Waddington and Roulet, 1996).

Median NEE was negative for all regions (Figure 6.17, Table 6.10). NEE was highest in the Peak District cores (i.e., a weaker C sink) which is largely due to the degraded cores being void of vegetation and thus, significantly reduced C uptake during photosynthesis. As these degraded cores may not be considered representative of degraded blanket bog more generally, fluxes were removed, and the data reanalysed. However, significant differences between regions remained the same. Sites in the Peak District were at the highest elevations and had the coolest average temperature (Table 6.1). Therefore, photosynthesis and respiration are impeded which is reflected in the lower fluxes. Minimum and maximum NEE flux were measured in Exmoor cores. In summer, there is a high C uptake by *Molinia* via photosynthesis whilst in winter, associated water table drawdown leads to an increase in decomposition due to inputs of labile OM in peat soils which is preferentially utilised by microbes. In addition, Exmoor had the lowest median NEE which is likely due to *Molinia* grass, which can develop an extensive root system along with high plant biomass, increasing C uptake via photosynthesis. When water tables are lowered due to drainage, large quantities of CO_2 are released (Rankin *et al.*, 2018)(which is also likely to occur when drawdown is vegetation mediated. This release following drawdown, however, may be offset by a high uptake of C via photosynthesis and a reduction in CH_4 emissions. In addition, *Molinia* are largely resistant to decay and thus contribute to slow decomposition rates (Bubier *et al.*, 1998), leading to lower R_{eco}.

CH_4 flux is known to be influenced by climatic variables in addition to vegetation community composition, and water table depth (Bhullar *et al.*, 2013; Ding *et al.*, 2003; Laine *et al.*, 2007a). It was therefore hypothesised that the wettest and warmest site (Exmoor), and sites characterised by higher sedge coverage (Peak District and Yorkshire) would have higher fluxes. Unexpectedly, cores from the Peak District had the lowest median CH_4 flux, which was assumed to be linked to the absence of vegetation on degraded cores. However, when these fluxes are removed from the data set, the median CH_4 flux from Peak District cores remains the lowest of all regions. This was unexpected given the significant association with sedge. Sedge-mediated CH_4 atmospheric transfer is a well-recognised CH_4 pathway in northern peatlands due to aerenchyma tissues allowing CH_4 to by-pass oxidation in the soil oxic-zone (Akhtar *et al*., 2021; Bhullar *et al*., 2013). In this study, CH_4 flux was positively correlated with air temperature (Figure 6.22), and therefore, lower CH_4 fluxes could be linked to a lower average temperature in this region. This suggests that climate conditions may exert a larger control over CH_4 emissions than vegetation community composition, however, this cannot be confirmed with data collected in this study.

C uptake via photosynthesis (gross primary productivity; GPP) and R_{eco} are positively correlated (Humphreys *et al*., 2006) along with temperature. In blanket bog ecosystems, GPP exceeds Reco and due to low temperatures and anoxic soil conditions (Humphreys *et al*., 2006) which contributes to functioning blanket bog being a net C sink. All GHG fluxes measured varied significantly with season with higher SR and R_{eco} and lower NEE when temperatures were highest (i.e., summer). This is consistently reported across the literature (e.g., (Bubier *et al*., 1998)). Surface temperatures have been shown to be more significant in affecting GHG flux in peatland compared to water table depth, however, water table depth has shown to be a good predictor nonetheless across a range of peatland vegetation communities (Bubier *et al*., 1998).

Evapotranspiration was radiatively driven at all sites but a decline in surface conductance with increasing water vapour deficit indicated physiological restrictions to transpiration, particularly at the peatlands with woody vegetation and less at the peatlands with 100 % *Sphagnum* cover (Humphreys *et al*., 2006).

Exmoor cores had the lowest median NEE over the course of this study and thus represents the largest C sink with respect to CO_2 fluxes. Exmoor is the warmest and wettest of all the regions in this study, but also differs significantly in its vegetation community composition. It is therefore difficult to disentangle the effects of both climate and vegetation. Exmoor may therefore represent a 'worst case scenario' under climate change whereby encroachment of vascular plants due to either changes in climate and/or degradation alters water table balance and/or C fluxes. In the context of GHG, Exmoor was shown to largely be a C sink and whilst a high *Molinia* coverage has implications for long-term C storage and water quality, it may be beneficial with regards to C uptake via vegetation.

6.5 Conclusion

Work presented in this chapter aimed to determine the effects of climatic variables on water quality and GHG fluxes in UK blanket bog.

This work showed that temperature exerts a significant control over GHG fluxes and water quality. Higher temperatures lead to increased DOC concentration and colour (UV_{254} and UV_{400} absorbance); whereby in summer collection months, water quality is lower compared to other seasons. Whilst a higher DOC concentration represents a higher coagulant demand, a high $SUVA_{254}$ indicates a high portion of the DOC is composed of hydrophobic DOC and therefore is amenable to coagulation. Exmoor on the other hand has a lower $SUVA_{254}$ compared to the other regions, suggesting a higher portion of DOC is composed of hydrophilic DOC which is not amenable to coagulation. It is likely that as this OM is more labile, it will be utilised within the catchment, prior to water reaching water treatment works. Lakes with longer residence times have been shown to have a higher buffer capacity, negating increases in DOC concentrations and water colour (Kohler, *et al*., 2013). Therefore, as frequency of drought increases, this may represent a significant source of DBP precursors. particularly when water is removed from reservoirs without sufficient time for microbial and UV degradation of OM which would normally occur. Samples from the Peak District cores (the coolest of all four regions) had the lowest DOC concentration. As vegetation in this region was more characteristic of blanket bog – and even with 100 % bare exposed peat on degraded cores – it is likely this was due to reduced rates of decomposition and OM turnover because of lower temperatures.

Hypothesis 1 was shown to largely be correct. *Molinia* was more significantly associated with cooler sites but was found in the warmest site (Exmoor), most likely due to high annual precipitation rates, despite deeper water table associated with *Molinia* grass. Hypothesis 2 was not proven. DOC concentrations were lower in cores from Exmoor with lower UV_{abs}, however, this would prove problematic during coagulation as part of the water treatment process as non-absorbing OM is not amenable to coagulation. Therefore, this DOC may represent a significant source of DBP precursor material. Hypothesis 3 was proven incorrect. R_{eco} was highest in Exmoor cores compared to the other regions, however had a significantly lower NEE flux (particularly in warmer periods), representing C uptake, despite deeper water tables because of high *Molinia* coverage. Hypothesis 4 was correct. CH_4 emissions were significantly higher from cores from Yorkshire and Scotland compared to the other two regions, which was attributed to higher sedge coverage. CH_4 flux was shown to positively correlate with temperature, and therefore flux is CH_4 flux is concluded to be a complex interplay between temperature, water table depth, and overlying vegetation community composition.

As discussed, it is difficult to disentangle the effects of climate and vegetation community composition upon water quality and GHG fluxes. The advantage of the mesocosm study design used in this work, is that environmental conditions were the same for all cores, and therefore the effects of vegetation on the provisioning of these ecosystem services could be determined. There were likely 'memory effects' of in-situ climate whereby microbial communities reflected region climatic conditions. To further understanding, results from this work could be coupled with microbial community analysis to further understand interactions between soil biota, vegetation, and hydrological processes occurring within peat soils.

7 Water Quality and drinking water treatment in UK blanket bog

7.1 Chapter summary

Dissolved organic carbon (DOC) in peatland draining waters can be problematic to drinking water treatment with increased concentrations leading to higher coagulant demand and disinfectant by-product (DBP) formation. Currently, there is limited understanding of the effects of blanket bog management and restoration on peat soil porewater chemistry, and subsequently drinking water treatment and DBP formation. The aim of this study was therefore to further understanding of DBP formation in peatland waters. Porewaters from mesocosm cores taken from four regions of UK blanket bog were studied for DBP-formation potential (trihalomethanes - THM) and amenability to traditional drinking water treatment methods. Predictive methods to assess a water's DBP- formation potential (DBPFP) were also explored. The most significant determining factor in the DBPFP of a water was found to be DOC concentration. UV_{254} and UV_{400} were significantly correlated with THM concentration (prior to coagulation) indicating that absorbance at these wavelengths can be a useful predictor of the THM – formation potential. Cores dominated by Molinia grass had lower DBPFPs but lower DOC removal by coagulation suggests waters from such areas would be problematic for drinking water treatment. Reducing DOC concentration in waters is the most effective way to reduce DBP formation and therefore any vegetation management and restoration methods which achieve this is beneficial in the context of drinking water treatment. As shown in previous chapters in this thesis, the effects of restoration and vegetation management vary between sites, and therefore optimal management in the context of improving water quality is site dependent.

7.2 Introduction

Blanket bogs are found at the headwaters of river catchments, and thus are significant sources of potable water (Peacock *et al*., 2015). Peatland water is coloured (reflecting its DOC content), and potentially contaminated with bacteria, so it is therefore treated with chlorine or chloroamines before use as potable water (Ritson *et al*., 2017). However, any residual organic matter will react with the chlorine and may form disinfectant by-products (DBPs) (Bond, 2009). These DBPs are problematic due to associated human health concerns, including genotoxicity and carcinogenicity (Benítez *et al*., 2021)and are therefore heavily regulated (Ritson *et al*., 2016) and a growing concern for utility companies, as precursor (i.e., DOC) load in raw waters is increasing (Kim *et al*., 2021).

DOC loading of peatland-draining waters has increased due to climate change (Ferretto *et al*., 2021a; Freeman *et al*., 2004; Lee *et al*., 2020; Salimi & Scholz, 2021; Xu *et al*., 2020a) and habitat degradation (Bussell *et al*., 2010), which has been linked to vegetation management (Clutterbuck & Yallop, 2010; Grayson *et al*., 2012). Therefore, understanding how DOC impacts disinfectant by-product formation potential (DBPFP) and which disinfectant by-products (DBPs) are produced during chlorination of waters has become increasingly important. Although various conventional water treatment technologies effectively removes most precursors,(Sadrnourmohamadi & Gorczyca, 2015), due to a mixture of autochthonous and allochthonous sources (Bond *et al*., 2012; Wetzel, 1992), in practice, not all precursor material can be removed (Chu *et al*., 2011). Therefore, controlling precursors at their sources could be a more effective and economically viable approach (Ritson *et al*., 2016). Studying the links between blanket bog land management, restoration, and climate with DBP formation could therefore provide useful information in developing more sustainable and effective water treatment moving forward (Chow *et al*., 2007) as this is currently not well understood.

DBPs represent a public health threat (Richardson *et al*., 2007), with studies indicating concentrations produced during drinking water treatment (DWT) are increasing due to a higher DOC load in raw waters (Williamson *et al*., 2022), likely resulting from raised temperatures (Fenner *et al*., 2021), an increase in the severity of drought events (Evans *et al*., 2005; Fenner & Freeman, 2011), and a reduction in atmospheric SO_4^{2-} deposition (Chapman *et al*., 2005; Evans *et al*., 2005). There are several classes of DBPs as detailed in Section 2.7, but in this study, due to time and financial constraints, the focus was on trihalomethanes (THMs) and haloacetic acids (HAAs).

Considering this, the major objectives of this chapter were to:

1) evaluate the quality (determined as the reactivity in forming DBPs) of DBP precursors and DOC removal efficiency in peatland soil porewaters;

2) to understand temporal and spatial variation of DBP precursors and,

3) to relate DBP concentrations to heather management, peatland restoration and climate in UK blanket bogs.

In addition, this chapter aimed to explore a predictive method to determine a water sample's risk at not being effectively treated via traditional coagulation methods.

Informed by data presented in Chapters 4, 5, and 6 in this thesis, the hypotheses to be tested were:

1) Due to higher DOC concentrations and colour, samples from uncut cores (i.e., those with tall heather plants), will have a higher DBP formation potential (DBPFP) compared to those from managed cores.

2) Samples from intact and restored cores will have a lower DBPFP than those from degraded cores.
3) UV absorbance parameters which are useful proxies for DOC characteristics will be useful predictors of DBPFP and % DOC removal.

7.3 Results

7.3.1 Trihalomethanes

A total of 88 raw porewater samples were analysed for THM formation potential. Bromoform, dibromochloromethane and bromodichloromethane were not detected in any of the samples analysed. Trichloromethane (TCM, known also as chloroform; $CHCl_3$) was detected in all samples and concentrations ranged from 38.4 – 6700.1 µg L^{-1} with a median of 1014.2 µg L^{-1} and a mean of 1251.3 ± 1094 µg L^{-1}.

TCM concentration was higher in warmer months demonstrating seasonality(Figure 7.1). TCM concentration was positively correlated with DOC concentration (Pearson's correlation = 0.50, $p < 0.01$; Figure 7.2) and DOC concentrations showed similar seasonal trends (Chapter 4, 5, and 6).

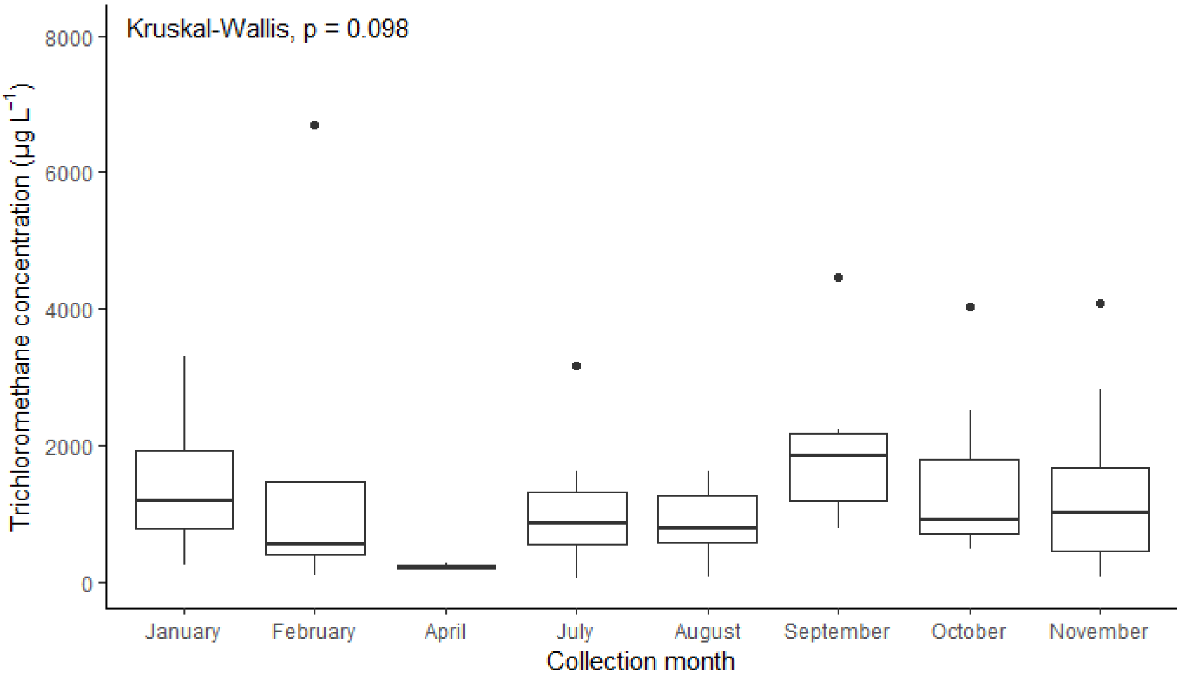


Figure 7.1 Mean trichloromethane concentration (µg L^{-1}) of raw mesocosm pore waters and sample collection month. Kruskal-Wallis significance test results are displayed. November 2021 and 2022 results combined.

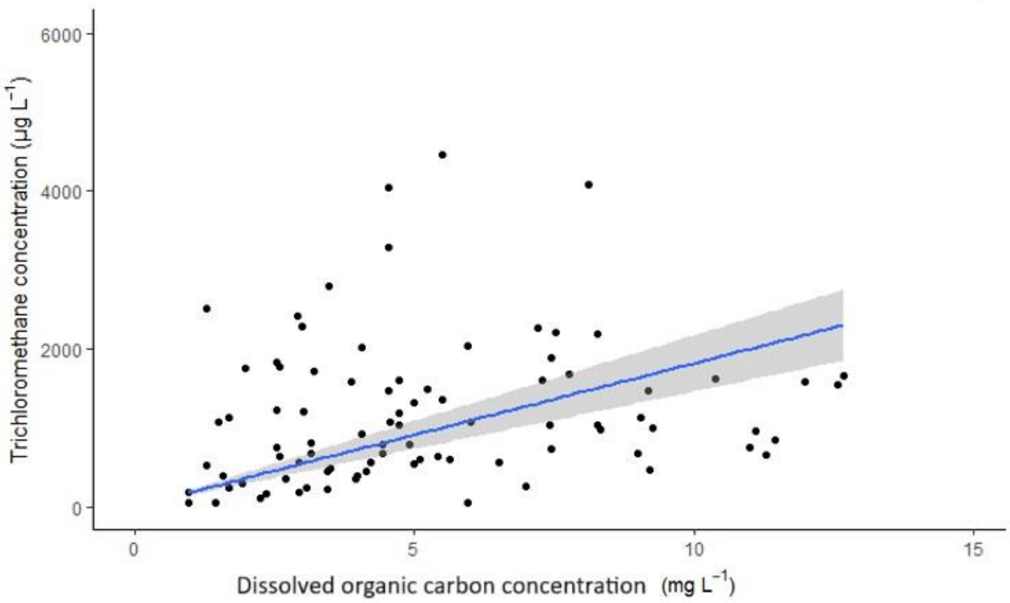


Figure 7.2 Dissolved organic carbon (mg L^{-1}) and post-chlorination TCM concentration (ug L^{-1}) mesocosm porewater samples. Pearson correlation coefficient presented. n = 88.

Mantel analysis (R package Vegan, Oksanen *et al*., 2022) indicated that a higher TCM concentration was not associated with dominant vegetation group (Mantel statistic: 0.03, p = 0.24) and there was no significant difference in TCM concentration between dominant vegetation groups (Kruskal Wallis = 87, df = 87, p = 0.48). The dominant vegetation group with the highest median TCM concentrations was sedge (1662 µg L^{-1}) And cores dominated by grass (i.e. *Molinea caerulea*) had the lowest TCM median concentration (298 µg L^{-1}) and the lowest DOC concentration, and typically were from Exmoor blanket bog.

7.3.1.1 Management

A total of 34 raw water samples from grouse managed blanket bogs were analysed for THMs. TCM concentration ranged from 264-6700 µg L^{-1} with a median of 1470 µg L^{-1} and a mean of 1619 ± 1325 µg L^{-1}. Samples from uncut cores had the lowest median TCM concentration (847 µg L^{-1}) whilst burnt samples had the lowest (1573 µg L^{-1}). However, there was no significant difference between TCM concentration between management regime (Kruskal Wallis chi-squared = 1.26, df = 2, p = 0.53) or site (Kruskal Wallis chi-squared = 1.78, df = 2, p = 0.41; Figure 7.3).

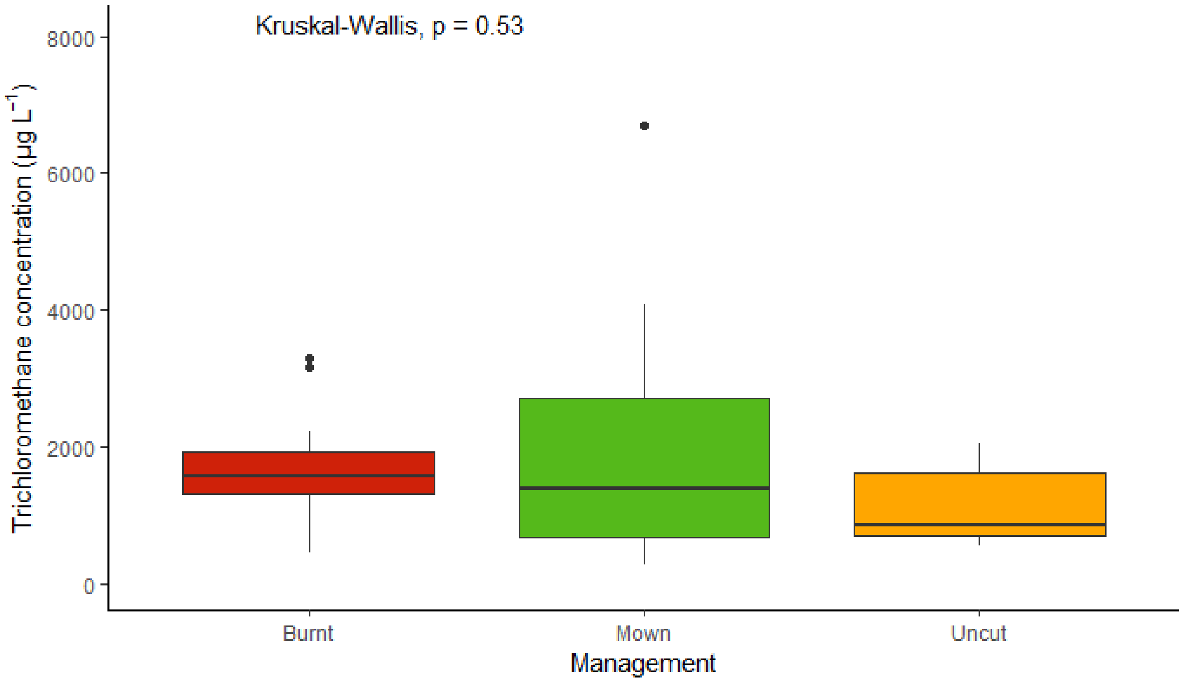


Figure 7.3 Trichloromethane concentration (µg L^{-1}) of raw mesocosm porewater samples following chlorination from three grouse blanket bog sites (Nidderdale, Mossdale, and Whitendale) under three management regimes (burnt, mown and uncut). n = 38.

7.3.1.2 Restoration

TCM concentration ranged from 38 – 4459 µg L^{-1} with a median of 847 µg L^{-1} and a mean of 1019 ± 854. µg L^{-1}. Samples from 10Y had the highest median concentration (1009 µg L^{-1}) compared to degraded core samples, which had the lowest median (519 µg L^{-1}). Overall, there was no significant difference between restoration status (Figure 7.4).

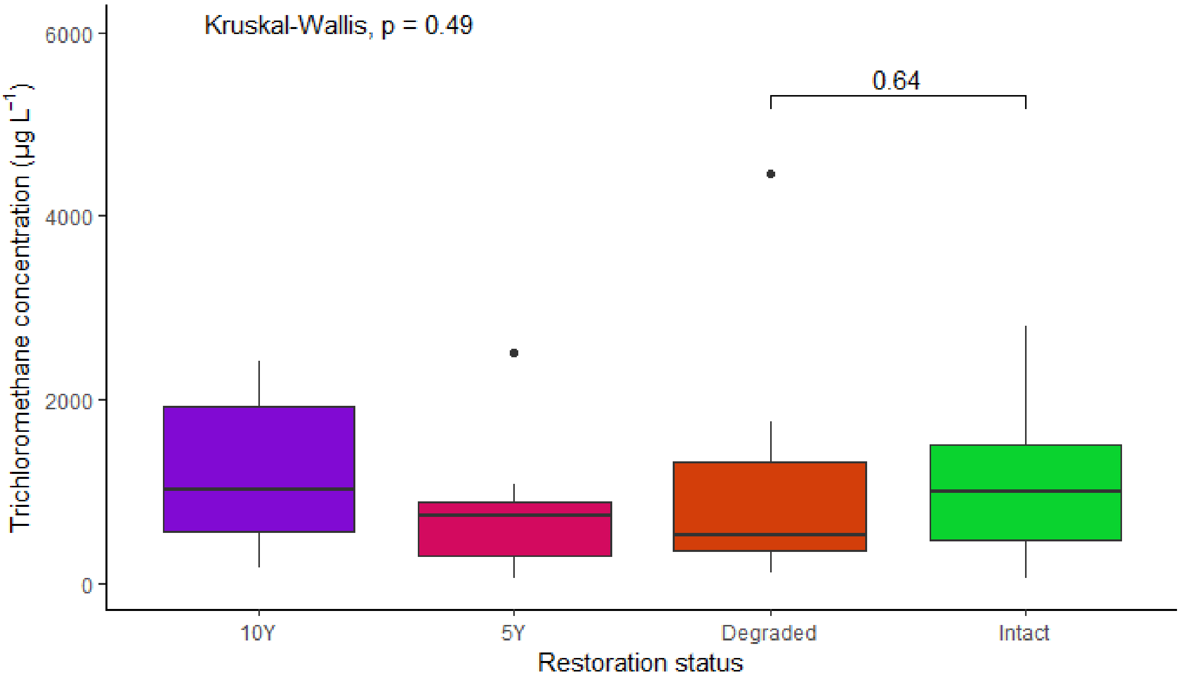


Figure 7.4 Trichloromethane concentration (µg L^{-1}) of mesocosm porewater samples pre-coagulation from three blanket bogs (in Scotland, the Peak District, and Exmoor) under three habitat conditions (10- and 5- year post restoration, intact, and degraded). Kruskal Wallis significance test result displayed. Significance testing result shown for degraded compared to intact cores.

7.3.1.3 Climatic region

Samples from Exmoor cores (dominated by *Molinia caerulea*) had the lowest median TCM concentration (519 µg L^{-1}) and were significantly lower compared with Yorkshire (Kruskal Wallis = 9.5, df = 3, p =0.02; pairwise Wilcoxon p =0.038; Figure 7.5). There were no significant differences in TCM concentrations between samples from the Peak District, Yorkshire, or Scotland.

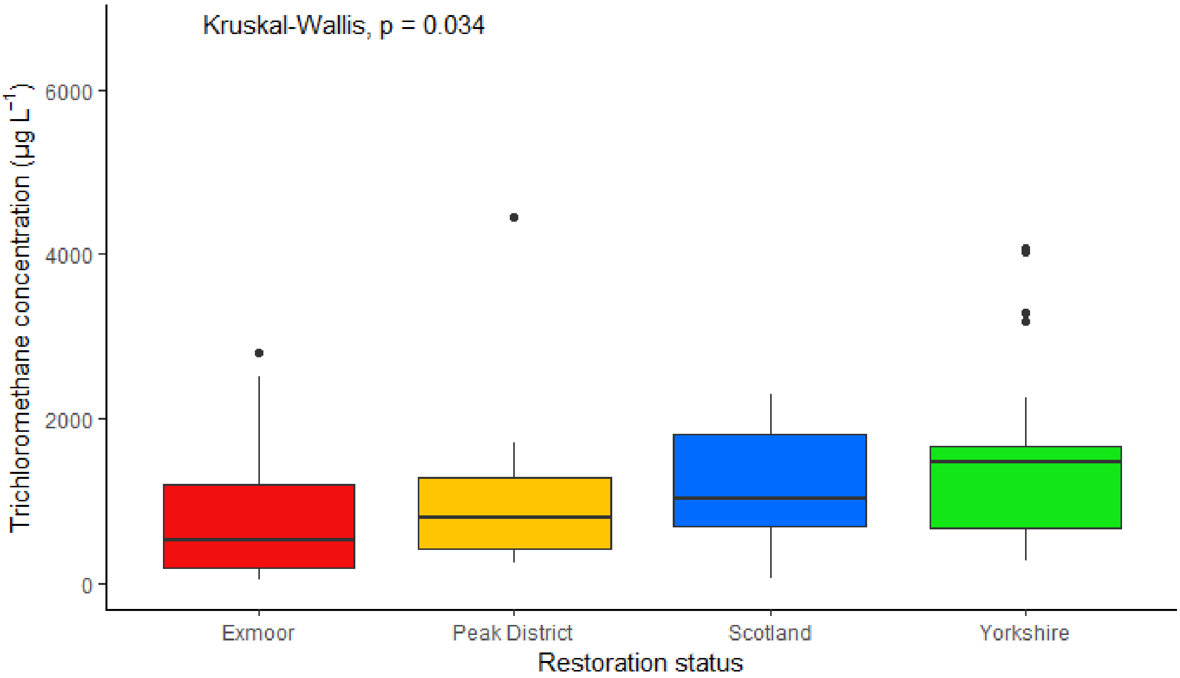


Figure 7.5 Trichloromethane concentration (µg L^{-1}) of mesocosm porewater samples post-chlorination from four blanket bog areas in the UK which represent a climatic spectrum. Statistical significance testing result shown. Outliers shown beyond the whiskers.

7.3.1.4 Trichloromethane formation potential

The formation of TCM (prior to coagulation) was significantly correlated with DOC concentration (Figure 7.2), and therefore trichloromethane formation potential (TCMFP) ($CHCl_3$ µg^{-1} DOC mg L^{-1}; as used by Galapate *et al*., (1999) and Gough *et al*., (2016)) may be a more useful indicator of the potential of a water to produce DBPs compared with TCM concentration.

TCMFP ranged from 9 – 1959 CH_3Cl µg^{-1} mg L^{-1} DOC with a median of 177 µg^{-1} CH_3Cl mg L^{-1} DOC and a mean of 279 ± 289 µg^{-1} CH_3Cl mg L^{-1} DOC. There were no significant differences in TCMFP between climatic regions (KW chi-squared = 0.1, df = 3, p = 0.99), nor management regime (KW chi-squared = 1.78, df = 2, p = 0.41), nor restoration status (KW chi-squared = 0.27, df = 3, p = 0.97). However, TCMFP did not differ significantly between vegetation groups (Figure 7.6 KW chi-squared p =

0.88)Mantel analysis indicated that vegetation cover (including all vegetation groups present) was not a significant driver of TCMFP (Mantel statistic = 0.07, p = 0.09).

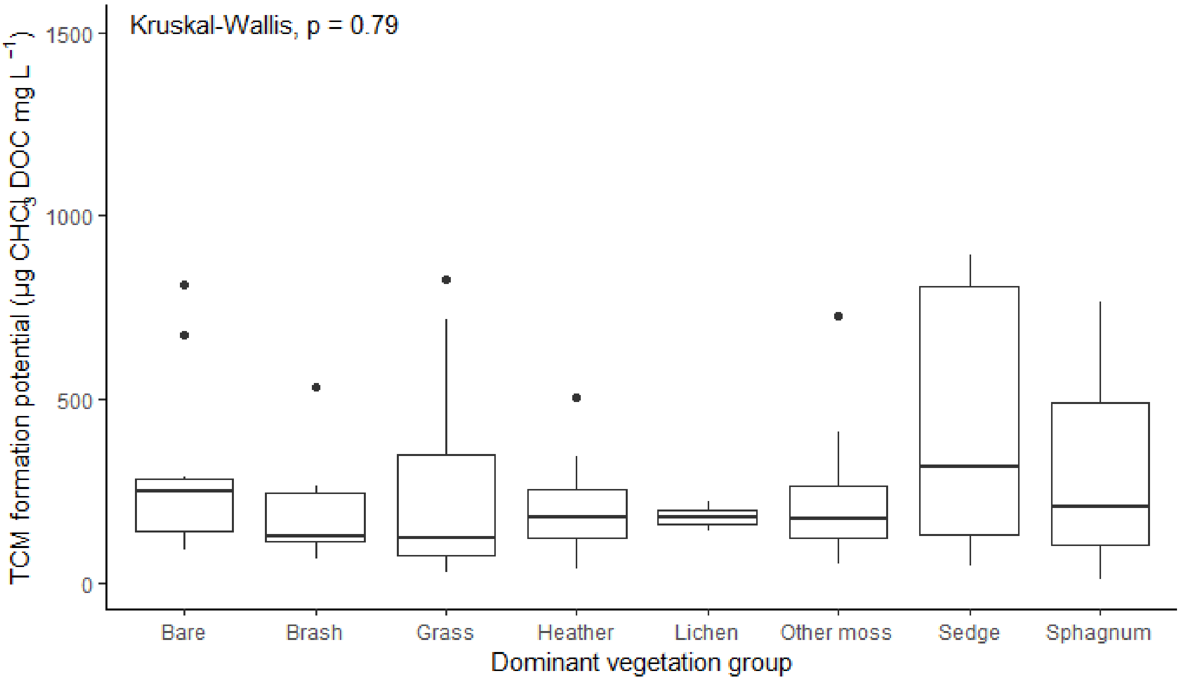


Figure 7.6 Trichloromethane formation potential (CHCl3 μg^{-1} DOC mg L^{-1}; TCMFP) and dominant vegetation groups from four blanket bog regions (Scotland, Yorkshire (including one site from the Forest of Bowland), the Peak District, and Exmoor). Significance testing result shown.

7.3.2 Haloacetic acids

HAAs were not detected in any of the samples analysed. The extraction method was repeated, and GC-MS settings adjusted to improve the methodology efficiency. This included shorterning initial hold times and gradients to reduce the overall method time and increase sample volume throughout. However, detection was not improved. As HAAs are a significant group of DBPs and the DOC concentration of the samples was in excess of waters treated within WTWs, it was thought unlikely that these compounds were not by-products of chlorination within the mesocosm porewater samples. It was therefore likely that the extraction method was not suitable for the samples being analysed. It would be useful to repeat this analysis with modifications to the extraction method however, due to time constraints, this was not done as part of this study.

7.3.3 Predicting disinfectant by-product formation

UV_{abs} is widely used as a proxy for the concentration and characteristics of OM, as detailed in Chapters 4, 5, and 6. Developing an effective proxy for DBPFP will be a useful tool in the prediction and prevention of the for DBPs and DBPs and could potentially lead to more sustainable and economically viable water treatment.

7.3.3.1 UV absorbance and DOC concentration as a proxy for disinfectant by-product formation potential

UV_{254} absorbance has been reported as being a good predictor of DBP formation (Edzwald *et al.*, 1985) and in this study, was found to be significantly correlated with TCM concentration prior to coagulation (Pearson correlation coefficient $R = 0.45$, $p < 0.01$; Figure 7.7). UV_{400} absorbance was also found to be significantly correlated with TCM concentration (Figure 7.8). These correlation coefficients are lower than commonly reported in the literature (e.g., Beauchamp, Dorea, Beaulieu, *et al.*, 2019; Roccaro & Vagliasindi, 2009). Correlation analyses were performed for key UV wavelengths and TCM concentration and where correlation was significant, a linear model was produced and tested for accuracy using various measures as detailed in Table 7.2. The predictive model using UV_{254} absorbance gives the lowest residual mean standard error (RMSE), but this is not significantly lower than DOC concentration or hazen predictive models. UV_{254} also gave the lowest mean difference between measured and predicted TCM concentrations. SUVA did not yield significant correlations, and therefore was not considered to be a useful predictor.

The variables discussed above however were not significant predictors of TCMFP. Correlation analysis indicated that only soil moisture and UV_{665} were significantly correlated with TCMFP. Similar trends were reported in Chapter 4 when considering differences in UV_{254} absorbance and SUVA between porewaters from peat soils under different management regimes. When absorbance was corrected for DOC concentration (as with TCM concentration and TCMFP), there was no longer a difference and, in this case, no longer a significant correlation.

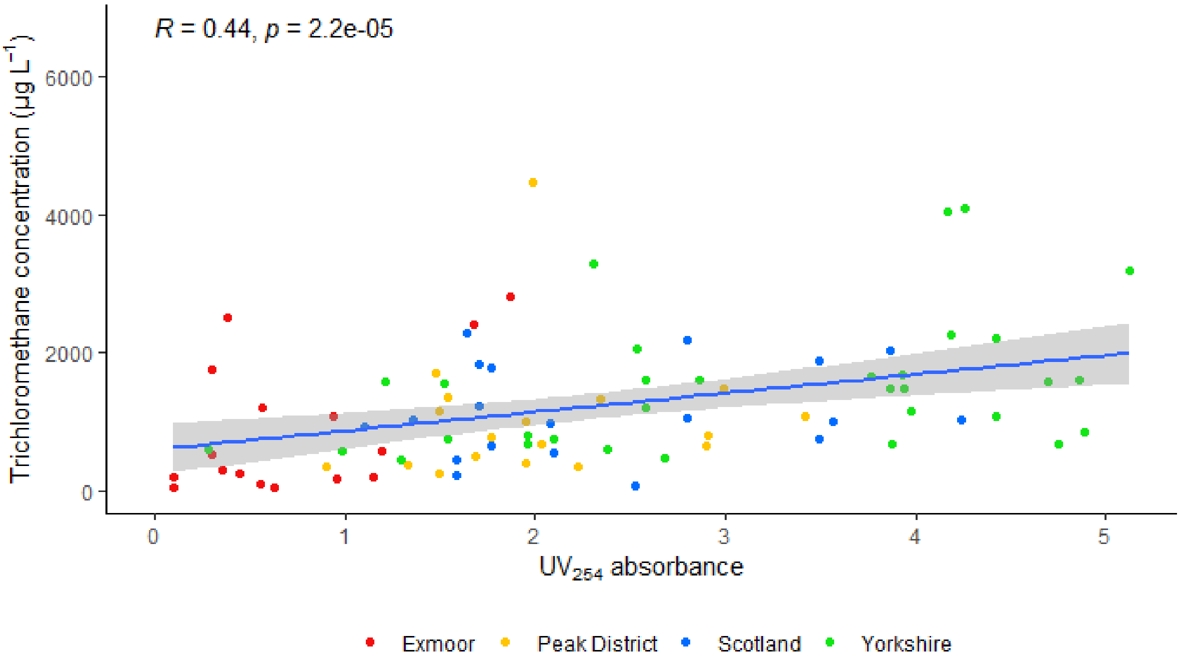


Figure 7.7 Spearman correlation analysis between UV_{254} absorbance and TCM concentration ($CHCl_3$ µg L^{-1}) of mesocosm pore water samples from four blanket bog areas (Exmoor, the Peak District, Yorkshire (which also includes one site from the Forest of Bowland), and Scotland). n = 88.

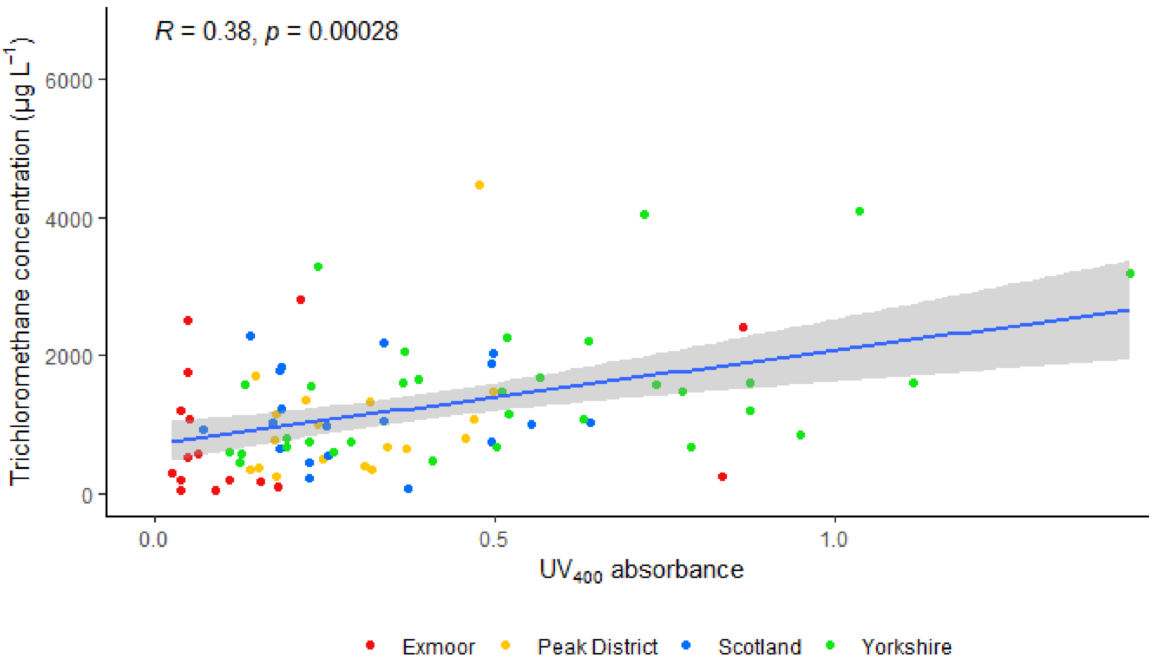


Figure 7.8 Spearman correlation analysis between UV_{400} absorbance and TCM concentration ($CHCl_3$ µg L^{-1}) of mesocosm pore water samples from four blanket bog areas (Exmoor, the Peak District, Yorkshire (which also includes one site from the Forest of Bowland), and Scotland). n = 88.

Table 7.1 Proxies for trichloromethane formation potential on raw waters collected from peat mesocosms. Spearman correlation analysis results presented. Significance value $p < 0.05$. Proxies which were significantly correlated to trichloromethane formation were then tested as predictive models (excluding UV_{400} as hazen is used instead). All lines of best fit were forced through 0,0. Mean difference refers to the mean difference between the measured and model-predicted trichloromethane concentration.

Proxy	R	P value	Model equation	Mean difference (µg L^{-1})	Nash-Sutcliffe	RMSE
DOC (mg L^{-1})	0.33	< 0.01	Y = 189.47x	-180.47	0.17	1264.91
UV_{254}	0.45	< 0.01	Y = 495.71x	--138.31	-0.006	1091.21
$SUVA_{254}$	-0.02	0.73	-	-	-	-
Hazen	0.39	< 0.01	Y = 227.92x	-270.14	-0.34	1258.57
UV_{400}	0.40	0.0002	Y = 2735x	-	-	-
E4:E6	-0.02	0.87	-	-	-	-

7.3.3.2 Differential UV absorption

For broad spectrum UV absorbance (UV_{abs}) 48 samples were analysed (all collected in November 2022 due to insufficient sample volume for previously collected samples). UV_{abs} at wavelengths 230 – 400 nm was an overall good predictor for TCM concentration (Pearson correlation ≥ 0.80 for all wavelengths). However, $UV_{230-400}$ absorbance was a poor predictor for TCM formation potential (corrected for by DOC concentrations (µg $CHCl_3^{-1}$ mg DOC L^{-1})) with correlation coefficients (R^2) ranging from -0.1 to -0.08.

Within the literature, the difference in UV_{272} (Δ_{272}) absorbance pre- and post- chlorination (2 hours following chlorination) has been reported as an indication of chlorine reactivity (Özdemir, Toröz and Uyak, 2013). In this study Δ_{272} (t=2) ranged from -0.60 – 0 with a median of - 0.03 and a mean of - 0.07 ± 0.11 and was a significant predictor of TCM concentration of samples pre-coagulation (Pearson correlation R = 0.81, p < 0.01; Figure 7.9). However, UV_{272} absorbance prior to chlorination was also a significant predictor for TCM concentration (Pearson correlation, R = -0.81, p < 0.01) and thus may be a more useful predictor for TCM formation.

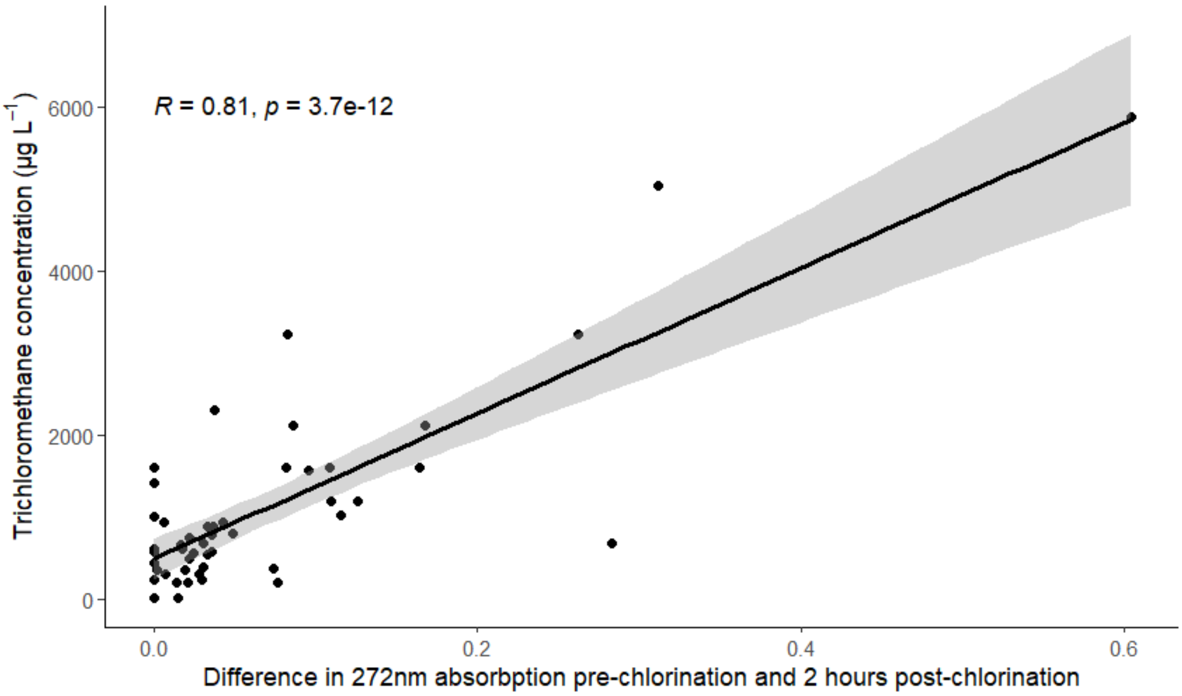


Figure 7.9 Difference in 272 nm absorbance in mesocosm porewater samples pre-chlorination and 2-hours post-chlorination as a predictor of trichloromethane concentration. Shaded area represents 95% error. Pearson correlation statistic shown.

However, it is important to note that within a WTW, waters may be chlorinated for an excess of two hours (Jenny Banks Technical Specialist, Yorkshire Water, per comms, 2023) and thus, to account for this, regular broad spectrum absorbance measurements (pre-chlorination, 2hr (t=2), 24hr (t=24), 48hr (t=48) and 120 hr (t=120) post chlorination) were taken.

The porewater samples collected in November 2022 were diluted 1:10 and measured for UV absorbance at 230-800 nm wavelengths prior to chlorination and then at 2 hr, 24 hr, 48 hr, and 120 hr post chlorination. Differential absorbance (ΔUV_{abs}) was always negative at 230-400 nm as the UV absorbance of OM decreased with chlorination (Özdemir *et al.*, 2013). The highest ΔUV_{272} values were observed at reaction times of 120 h (-0.20 ± 0.16), demonstrating that the magnitude of the differential spectra developed with increasing chlorination rection time, which is consistent with a previous study (Özdemir *et al.*, 2013). Abs_{272} significantly decreased between selected time intervals (Kruskal Wallis chi-squared = 31.411, df = 4, p-value < 0.01). However, absorbance pre-chlorination was found to be the most significant predictor of trichloromethane concentration (Table 7.4) and thus, measuring a raw water at 272 nm is likely a more optimal predictive tool rather than measuring UV_{abs} at intervals post-coagulation.

Table 7.2 Models of the difference in UV272 absorbance (Δ_{272}) and trichloromethane (TCM) concentration at the various time points where UV absorbance was measured. Start time (0 hours) represents absorbance pre-chlorination. Models were all linear. y = TCM concentration (µg L^{-1}) and x = 272 nm absorbance.

Time (hours)	Model equation	R value	Spearman correlation coefficient	RMSE of predicted vs measured TCM concentration
0	y = 3089.7x – 260.71	0.76	< 0.01	609.44
2	y = 3841x – 349.91	0.73	< 0.01	719.81
24	y = 4028.2x – 204.05	0.73	< 0.01	795.55
48	y = 4080.6x – 2.7674	0.65	< 0.01	876.39
120	y = 4148.1x + 97.024	0.66	< 0.01	840.56

ΔUV_{abs} was shown to increase (i.e. the difference between pre-chlorinated sample absorbance and at the various time intervals post chlorination increased, and thus became more negative over time) with increased time following chlorination (Figure 7.10). The largest ΔUV_{abs} was at longer wavelengths, but the ΔUV_{abs} between the time intervals at these wavelengths were smaller than at shorter wavelengths. The spectra exhibited the least negative rate decline at around 270 nm – 290 nm, which is also reported within the literature (Özdemir *et al.*, 2013).

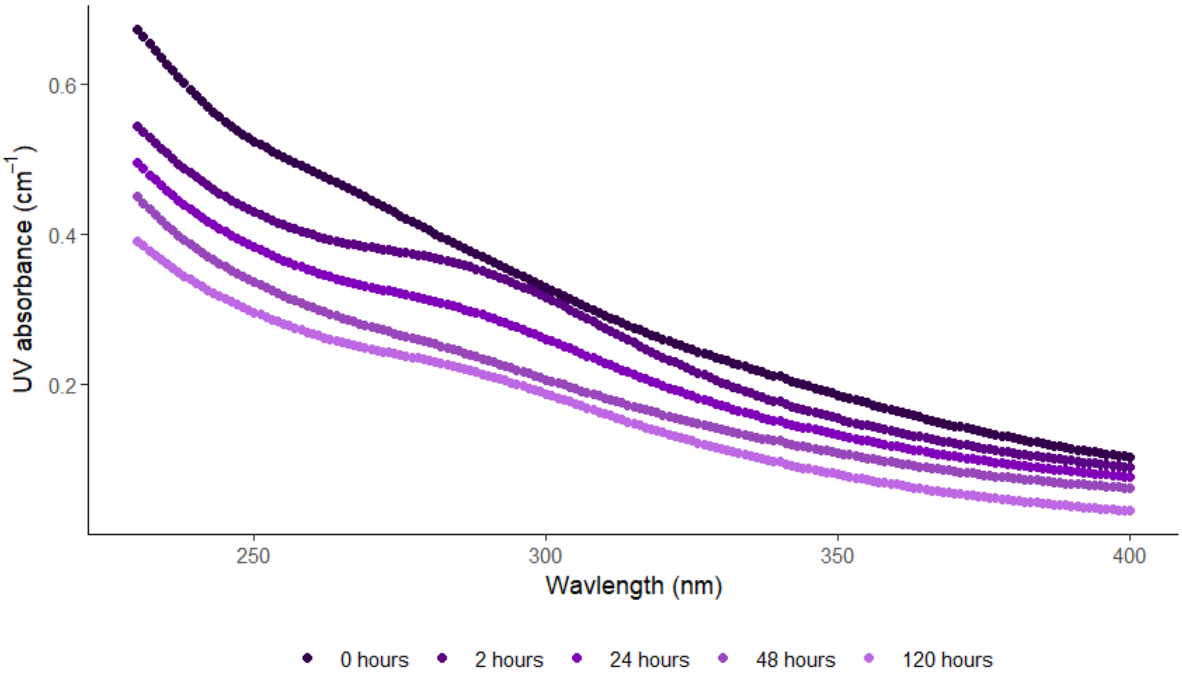


Figure 7.10 Differential absorbance for $UV_{230-400}$ for mesocosm porewaters 2 hours, 24 hours, 48 hours, and 120 hours post-chlorination. Absorbance for each wavelength is the mean absorbance for all samples analysed.

7.3.3.3 Generalised linear modelling for trichloromethane predictors

A GLM was fitted to the data to determine the strongest predictors for TCM concentration. Air and soil temperature and light levels were used rather than collection month as an indicator for seasonality. The initial model consisted of monthly average air temperature, monthly average soil temperature, sum of monthly light levels, DOC concentration and % vegetation coverage. Variables with VIF values > 5 were sequentially removed until all VIF values < 4; monthly average air,light level and % bare ground coverage were removed in this way. A model was then obtained with 8 variables: DOC concentration, % *C. vulgaris*, % *Sphagnum* spp., % brash, % shrub, % sedge, % Other moss and % grass coverage. Of these variables, DOC concentration, air temperature, and % brash were significant drivers (seen in Figure 7.11); correlation between TCM and DOC shown in Figure 7.2). The final model is detailed in Table 7.4

Table 7.3 Model parameters for generalised linear model (GLM) for trichloromethane predictors. RMSE = residual mean standard error.

Coefficients	Estimate	Std. Error	T value	p-value	VIF	AIC	Model RMSE	R^2
Intercept	1481.21	326.505	4.537	< 0.0001	-	1454.55	982.9	0.27
Dissolved organic carbon concentration (mg L^{-1})	108.015	21.123	-2.413	**< 0.01**	1.21			
Air temperature (°C)	-50.97	21.123	-2.413	**0.01**	1.06			
% *Sphagnum* spp.	-4.922	5.508	-0.894	0.37	1.20			
% Brash	-14.916	6.646	-2.244	**0.02**	1.21			
% Shrub	5.789	13.260	0.437	**0.66**	1.02			
% Other moss	13.95	7.64	1.83	0.07*	1.60			
% Grass	-20.82	8.90	-2.34	**0.02**	1.65			

7.3.4 Comparing DOC concentrations pre- and post-coagulation

To compare efficiency of coagulation in the removal of DOC from porewaters, 81 samples underwent coagulation. Prior to coagulation, DOC concentration of samples tested ranged from 8.9 – 261.8 mg L^{-1} with a median of 55.8 mgL^{-1} and a mean of 74.7 ± 55.9 mg L^{-1}. All samples underwent a 1:10 dilution to reflect the concentrations of water typically undergoing coagulation in DWTPs, and to reduce the additional volume of the coagulant solution being added to the samples. Thus prior to coagulation, DOC concentration of these diluted samples ranged from 0.90 – 26.18 mg L^{-1}. DOC concentration decreased following coagulation in all samples, with a mean % removal efficiency of 46 ± 24.6%. DOC concentration in samples post-coagulation and removal was significantly lower than pre-coagulation (Mann Whitney Wilcoxon, $W = 5109$, $p < 0.001$; Figure 7.11). % Removal efficiency ranged from 1.1 – 86.6 %. Removal efficiency was positively correlated with sample DOC concentration (Spearman's rank correlation; $R = 0.49$, $p < 0.01$) and Hazen (Pearson's correlation, $R = 0.27$, $p < 0.01$).

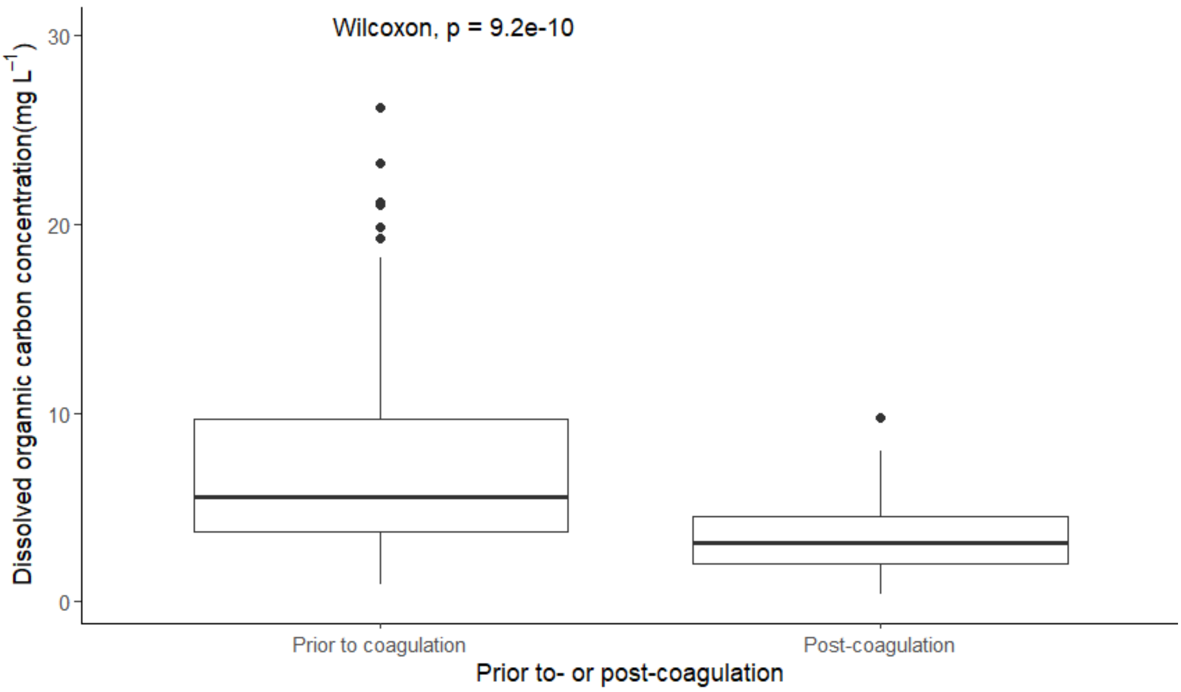


Figure 7.11 Comparison of dissolved organic concentration of mesocosm porewaters prior to- and post-coagulation mesocosm porewater samples. Mann Whitney Wilcoxon significance testing result shown. Outliers shown beyond the whiskers.

7.3.4.1 Management

There was no significant difference between management regime (Kruskal-Wallis = 0.76, df =2, p = 0.76), although porewaters from burnt cores had the highest median % DOC removal, whilst uncut cores had the lowest (56.78 % compared to 52.60 %; Figure 7.12). However, mown cores showed a much narrower range in % DOC removal.

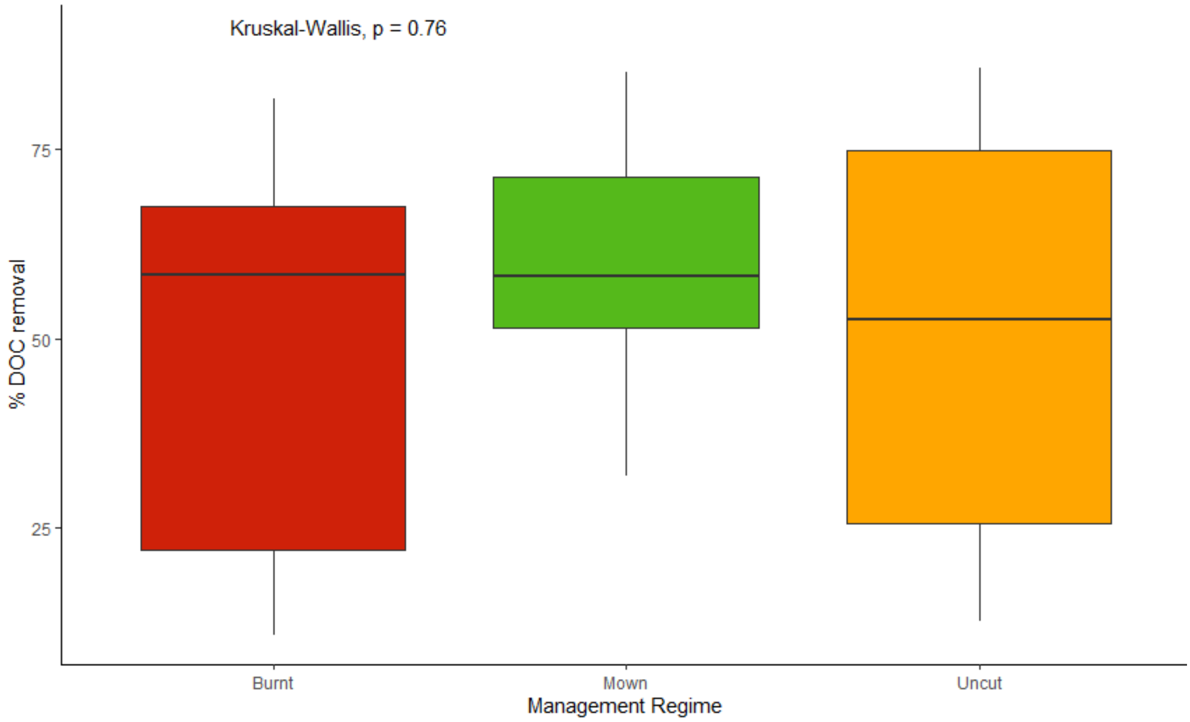


Figure 7.12 Percentage dissolved organic carbon (mg L^{-1}) removal following coagulation of mesocosm pore waters from three grouse-blanket bogs (Nidderdale, Mossdale, and Whitendale) under three management regimes (burnt, mown, and uncut). Kruskal Wallis significance test result shown.

7.3.4.2 Restoration

Porewaters from intact cores had the highest median % DOC removal, compared to 5Y post-restoration which had the lowest (55.79 % compared to 31.76 %); however, this difference was not significant (ANOVA, F = 1.38, df = 3, p = 0.26; Figure 7.13).

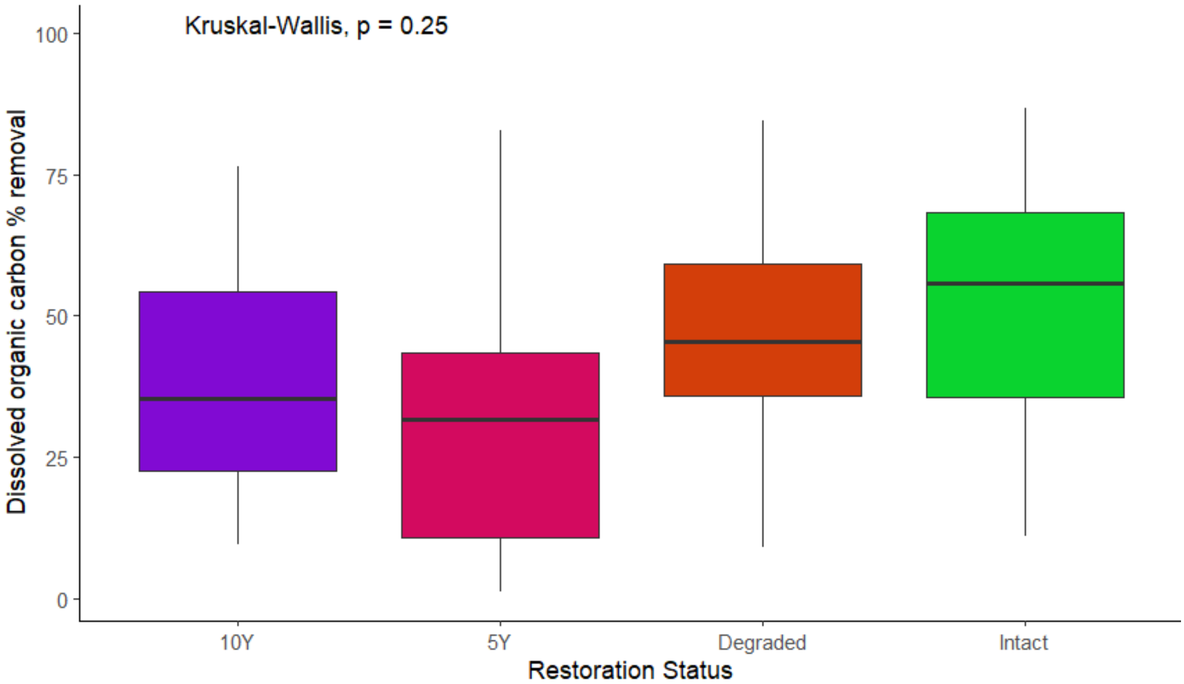


Figure 7.13 Percentage dissolved organic carbon (DOC; mg L^{-1}) removal following coagulation of mesocosm porewaters from three blanket bog areas (Scotland, the Peak District and Exmoor) under four habitat conditions (10- and 5-year post restoration, degraded, and intact). Significance testing result shown.

7.3.4.3 Climatic regions

Porewaters from Yorkshire cores had a significantly higher DOC % removal, compared to Exmoor which had the lowest (53.6 ± 23.9 % compared to 35.8 ± 25.2 %; $p < 0.05$, Figure 7.14).

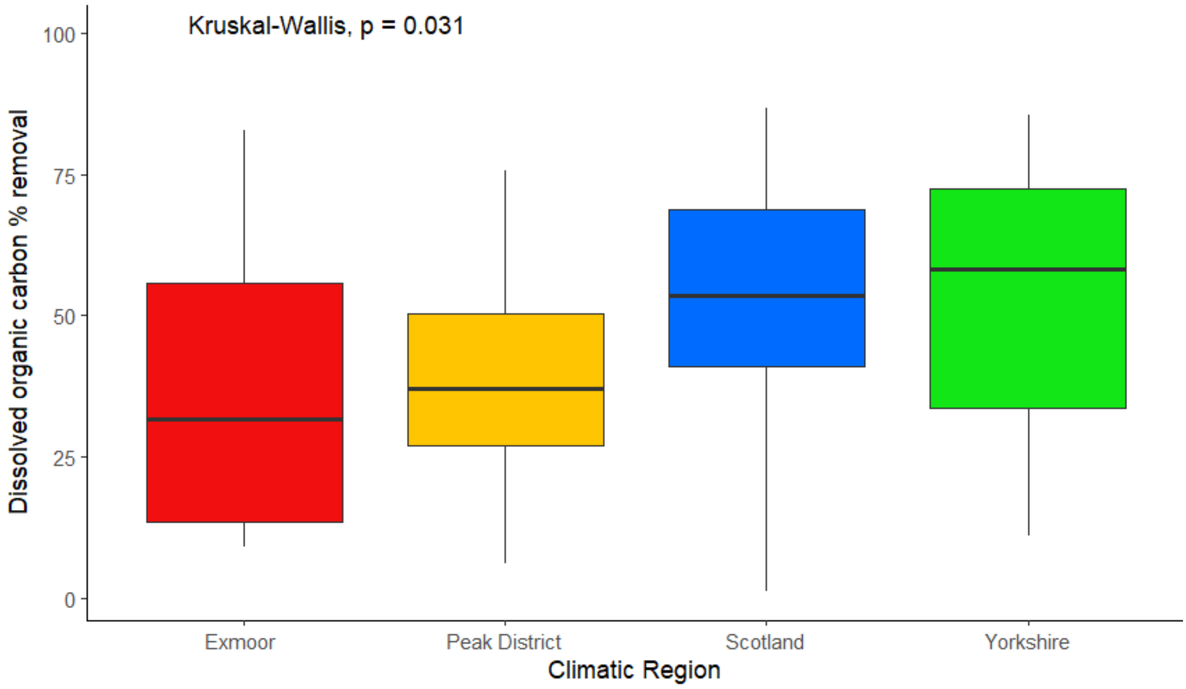


Figure 7.14 Percentage dissolved organic carbon (DOC; mg L^{-1}) removal following coagulation of mesocosm porewaters from four climatic regions (Scotland, the Peak District, Yorkshire, and Exmoor). Significance testing result shown.

7.3.4.4 DOC removal and vegetation

Mantel analysis indicated that vegetation was not a significant driver of % DOC removal (Mantel statistic r = -0.02, p 0.73), and % DOC removal was shown to not differ significantly between dominant vegetation groups (KW chi-squared = 80, p = 0.48; Figure 7.15). Median % DOC removal was highest in samples from cores dominated by sedge (67.7 %) and lowest in cores dominated by other moss (31.9 %), albeit with a small sample size (3 samples). It is also important to note that whilst cores dominated by brash had a high % DOC removal, only 2 samples were tested.

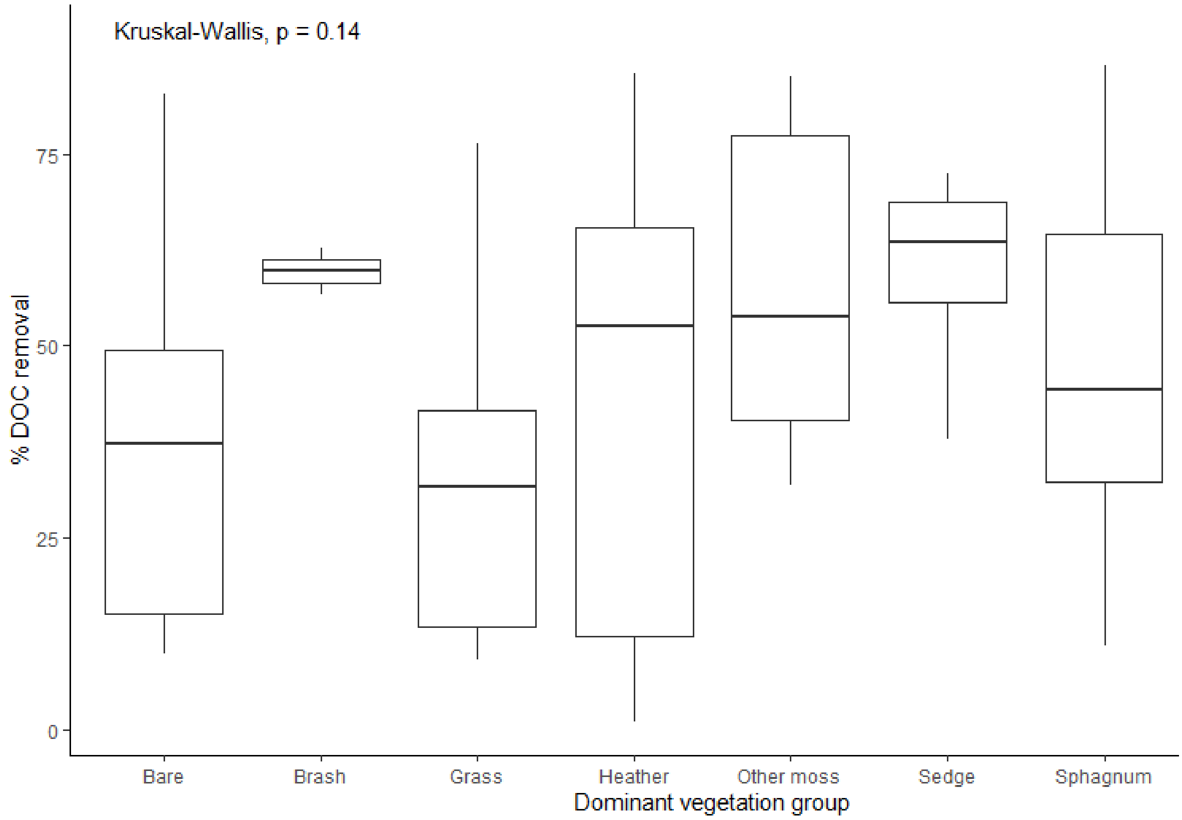


Figure 7.15 Dissolved organic carbon removal efficiency (%) and peat mesocosm core dominant vegetation groups. Results from cores dominated by lichen and shrubs were removed as there was only one sample per vegetation group. Kruskal Wallis test p-value displayed. n = 79.

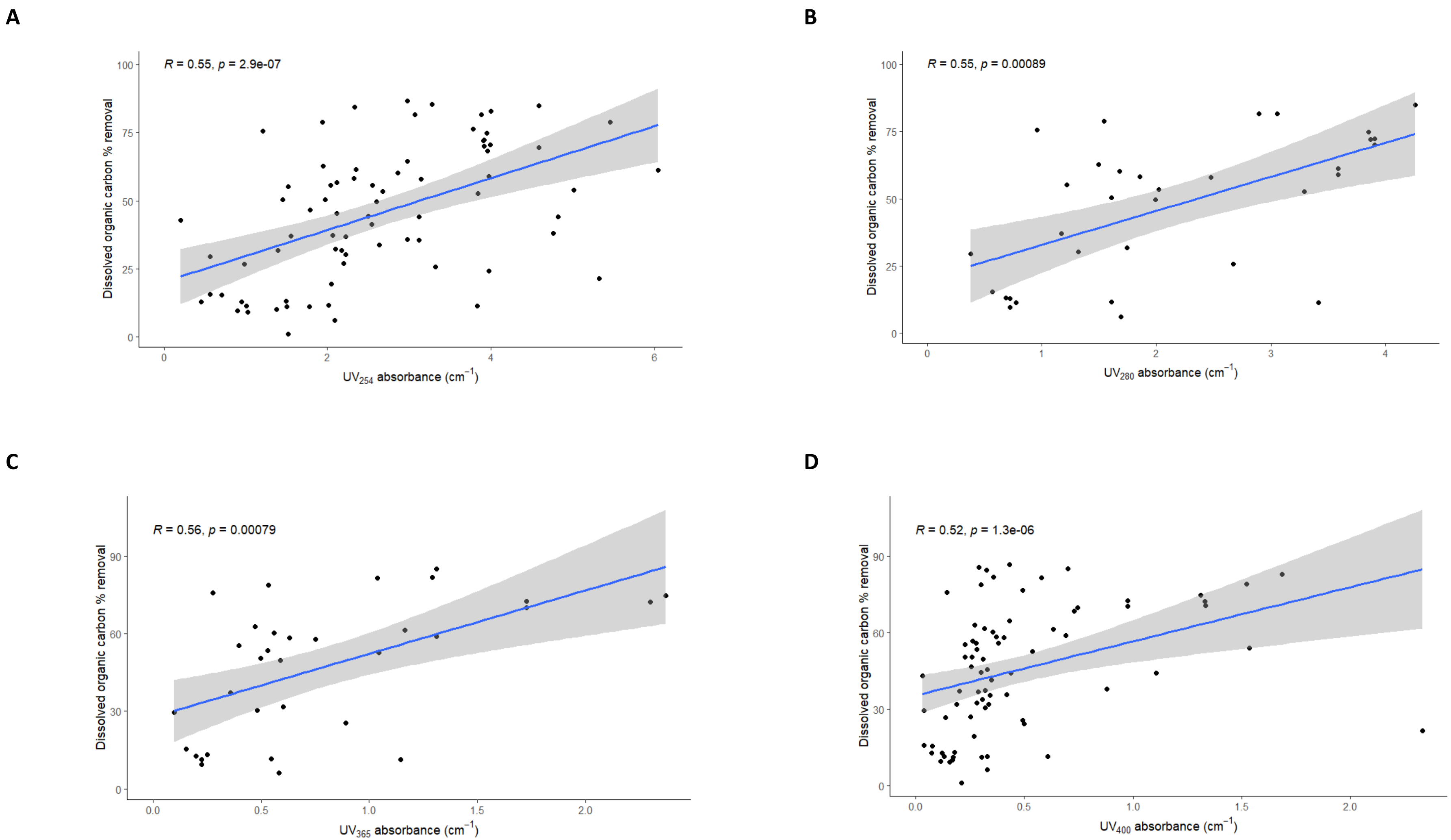
7.3.4.5 Predicting DOC removal efficiency

Hydrophobic molecules are known to be more amenable to coagulation than hydrophilic counterparts (Edzwald, 1993) and thus waters with an organic fraction dominated by such molecules should show a higher % DOC removal. Waters with a dominant hydrophobic organic fraction also exhibit high absorbance at key UV wavelengths (Table 2.17). Therefore, UV absorbance was hypothesised to be a good predictor of coagulation efficiency.

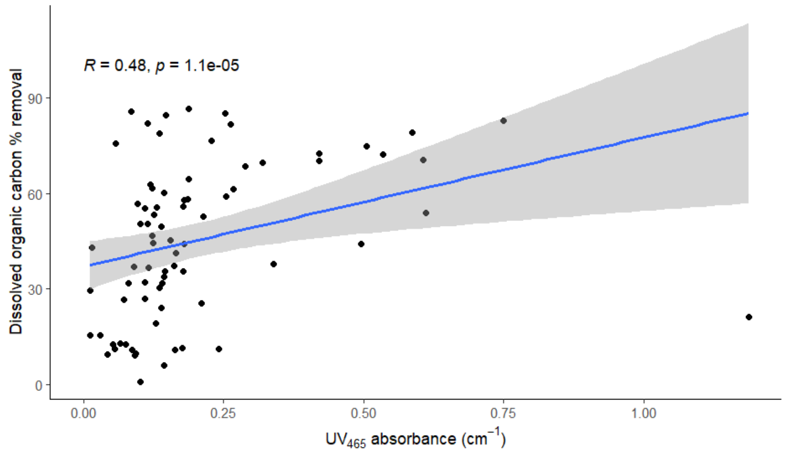
Table 7.4 Key ultraviolet (UV) wavelengths and correlation coefficient (R^2) with % dissolved organic carbon (DOC; mg L^{-1}) removal. P significance value 0.05. In the linear model, y refers to % DOC removal and x refers to the UV absorbance at the wavelength indicated.

Wavelength (nm)	R^2 value	P value	Linear model	*n =*
254	0.55	< 0.01	y = 9.5448x + 20.132	76
280	0.55	< 0.01	y = 12.689x + 20.104	33
365	0.55	< 0.01	y = 24.506x + 27.708	
400	0.52	< 0.01	y = 21.26x + 35.238	76
465	0.48	< 0.01	y = 12.689x + 20.104	
665	0.28	0.01	y = 80.037x + 40.756	

Absorbance wavelengths tested were significantly correlated with % DOC removal and were thus good predictors of coagulation efficiency as hypothesised (Table 7.5; Figure 7.16). Lower wavelengths were more accurate proxies of % DOC removal with R = 0.55, p <0.01. $SUVA_{254}$ on the other hand did not significantly correlate with % DOC removal and was thus a poor predictor of coagulation efficiency (R^2 = -0.18, p = 0.13).


A
R = 0.55, p = 2.9e-07
Dissolved organic carbon % removal
UV254 absorbance (cm−1)
B
R = 0.55, p = 0.00089
Dissolved organic carbon % removal
UV280 absorbance (cm−1)
C
R = 0.56, p = 0.00079
Dissolved organic carbon % removal
UV365 absorbance (cm−1)
D
R = 0.52, p = 1.3e-06
Dissolved organic carbon % removal
UV400 absorbance (cm−1)

E



F

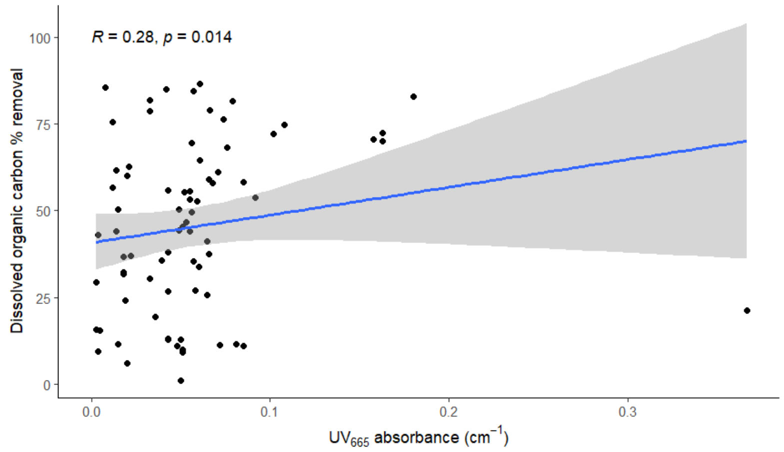


Figure 7.16 Correlation between UV absorbance of A) 254 nm, B) 280 nm, C) 365 nm, D) 400 nm, E) 465 nm, and F) 665 nm and percentage dissolved organic carbon removal (compared to pre-coagulation). Correlation analysis results shown. Line of best fit shown. Shaded area represents 95% confidence interval.

7.3.5 THM production post-coagulation

THM_4 concentration post-coagulation was tested in 40 samples dependent on available sample volume after analysis previously described in this chapter. As with the raw water samples, TCM was the only THM_4 detected and was presented in all samples. TCM concentration ranged from 431.1 – 647.6 µg L^{-1} with a mean of 514.1 ± 55.3 µg L^{-1}. TCM concentrations in all samples post-coagulation were significantly lower than pre-coagulation (Mann-Whitney, W = 40, $p < 0.01$; Figure 7.17). However, all samples exceeded the regulatory limit of 100 µg L^{-1} and post-coagulation TCM was not significantly correlated with DOC concentration post-coagulation (Spearman's correlation = 0.05, p = 0.72), unlike prior to coagulation.

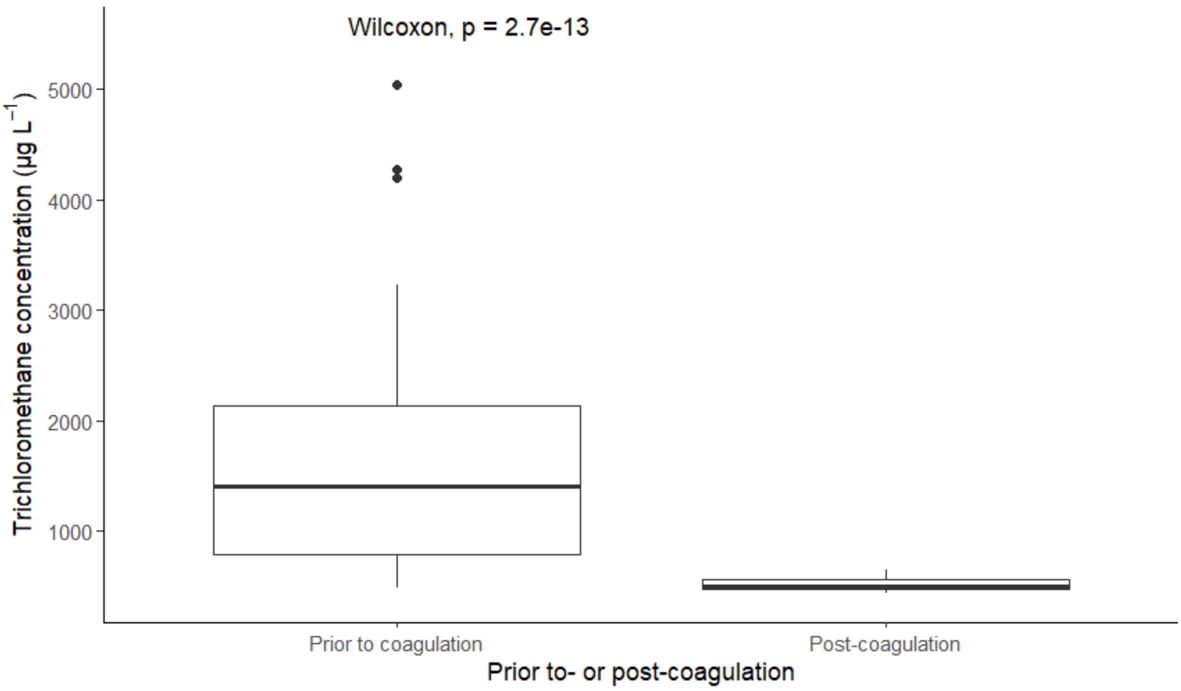


Figure 7.17 Trichloromethane concentration in mesocosm porewaters prior to- and post-coagulation. Mann Whitney Wilcoxon significance testing result shown. Outliers shown beyond the whiskers.

The mean percentage reduction in TCM concentration post-coagulation was 54.7 ± 25.5 % and was highest in cores dominated by brash and lowest in cores dominated by *Sphagnum*. However, % reduction did not differ significantly between vegetation groups (KW chi-squared = 6.55, df = 7, p = 0.48; Figure 7.18 and Figure 7.19). Vegetation was not found to be a significant driver of any differences in TCM concentrations post-coagulation (Mantel statistic; r = 0.02, p = 0.32) but was a significant driver in % reduction in TCM formation post-coagulation (Mantel statistic; r = 0.13, p = 0.02).

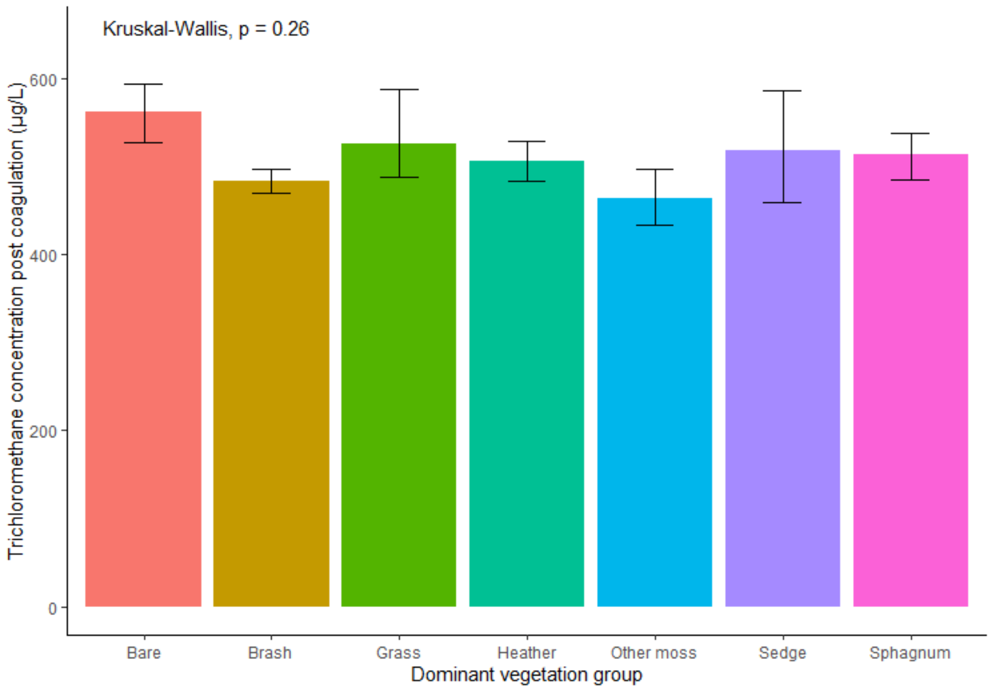


Figure 7.18 Mean trichloromethane (TCM) concentration of peat mesocosm pore waters from four areas of blanket bog (Exmoor, the Peak District, Yorkshire (including one site from the Forest of Bowland), and Scotland) post-coagulation and core dominant vegetation group. Error bars show standard deviation.

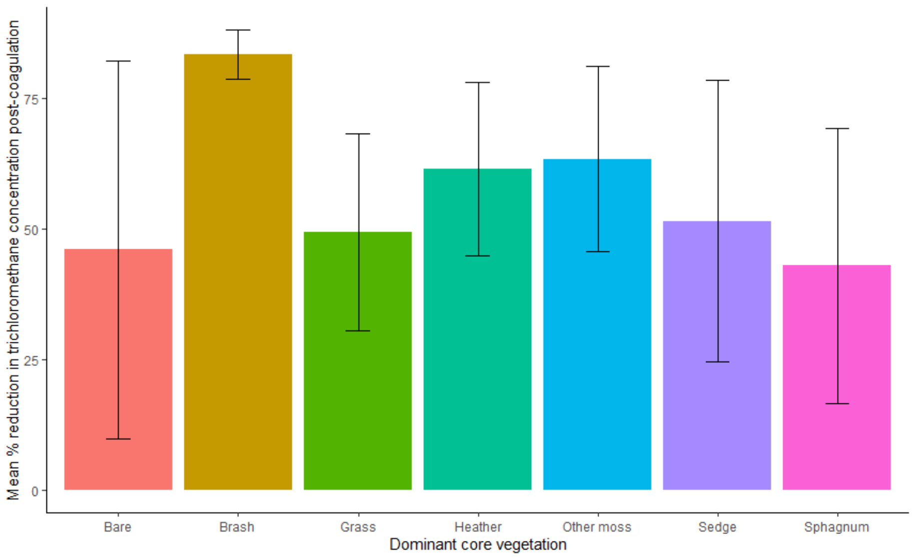


Figure 7.19 Mean reduction in trichloromethane (TCM) concentration of peat mesocosm pore waters from four areas of blanket bog (Exmoor, the Peak District, Yorkshire, and Scotland) following coagulation and core dominant vegetation group. Error bars show standard deviation.

TCM concentrations post-coagulation did not differ between restoration status (Kruskal Wallis chi-squared = 3.24, df = 2, p = 0.36), management regime (Kruskal Wallis chi-squared = 0.5, df = 2, p = 0.78), nor climatic region (Kruskal-Wallis chi-squared = 3.44, df = 3, p = 0.33).

7.3.6 Characterisation of porewater dissolved organic carbon

The characterisation of the nature of the OM which constitutes DOC in peatland draining waters would provide some insight into processes which increase DBPFP. At the start of this project, it was hoped that this would form the bulk of this chapter, however due to Covid-19 and other constraints, this work is fairly limited. Therefore, it is hoped that the following results can inform future work post-PhD.

7.3.6.1 Acetate and Formate

Acetate was present in the majority of peat pore water samples (87 out of 98 analysed) and had a range of 0.0018 – 11.82 mg L^{-1} with a median of 0.13 ± 0.19 mg L^{-1} and a mean of 1.07 ± 2.21 mg L^{-1}. Acetate and formate concentration were significantly positively correlated with DOC concentration ($R = 0.30$, $p < 0.05$ and $R = 0.51$, $p < 0.05$ respectively).

7.3.6.1.1 Management

The 38 pore water samples from generally heather-dominated (grouse-moor managed) mesocosms were analysed for acetate and formate concentrations. Acetate was detected in 37 samples and had a range of 0.006 – 9.3 mg L^{-1} with a median of 0.16 ± 0.2 mg L^{-1} and a mean of 1.13 ± 2.09 mg L^{-1}. Formate was detected in all 38 samples, with a range of 0.0081 – 1.3 mg L^{-1} with a median of 0.8 ± 0.09 mg L^{-1} and a mean of 0.2 ± 0.3 mg L^{-1}.

There were no significant differences in acetate or formate concentration between management regimes (Kruskal Wallis chi squared = 1.47 and 0.33 , df = 2, p = 0.48 and p = 0.85, respectively). However, median concentration for both precursors was highest in burnt cores (Figure 7.20). Acetate and formate concentration did not differ significantly between management sites (Kruskal Wallis chi-squared = 1.61 and 2.01, df = 2, p = 0.45 and p = 0.37, respectively).

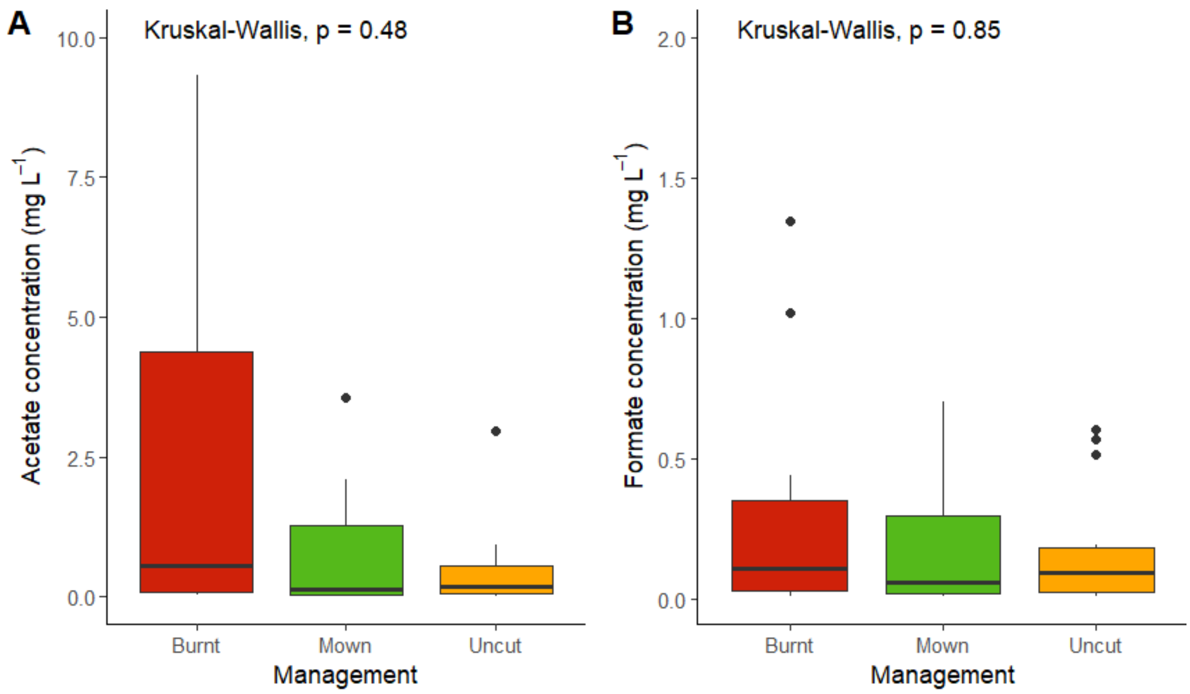


Figure 7.20 Acetate (**A**) and formate (**B**) concentration (mg L^{-1}) in mesocosm pore water samples from three grouse-blanket bog (Nidderdale, Mossdale, and Whitendale) under three management (burnt, mown and uncut) regimes. Significance testing result shown. Outliers shown beyond the whiskers.

7.3.6.1.2 Restoration

59 pore water samples from degraded-restored mesocosms were analysed for acetate and formate concentrations.

Acetate was detected in 49 samples and had a range 0.0018 – 11.82 mg L^{-1} with a median of 0.11 ± 0.15 mg L^{-1} and a mean of 1.02 ± 2.31 mg L^{-1}. Formate was detected in 58 samples, with a range of 0.0026 – 1.72 mg L^{-1} with a median of 0.01 ± 0.01 mg L^{-1} and a mean of 0.19 ± 0.38 mg L^{-1}. There were no significant differences in acetate or formate concentration between restoration status (Kruskal Wallis chi squared = 2.89 and 5.37 , df = 2, p = 0.41 and p = 0.15, respectively; Figure 7.21). Acetate median concentrations were highest in 10Y post-restoration samples whilst formate was highest in intact cores.

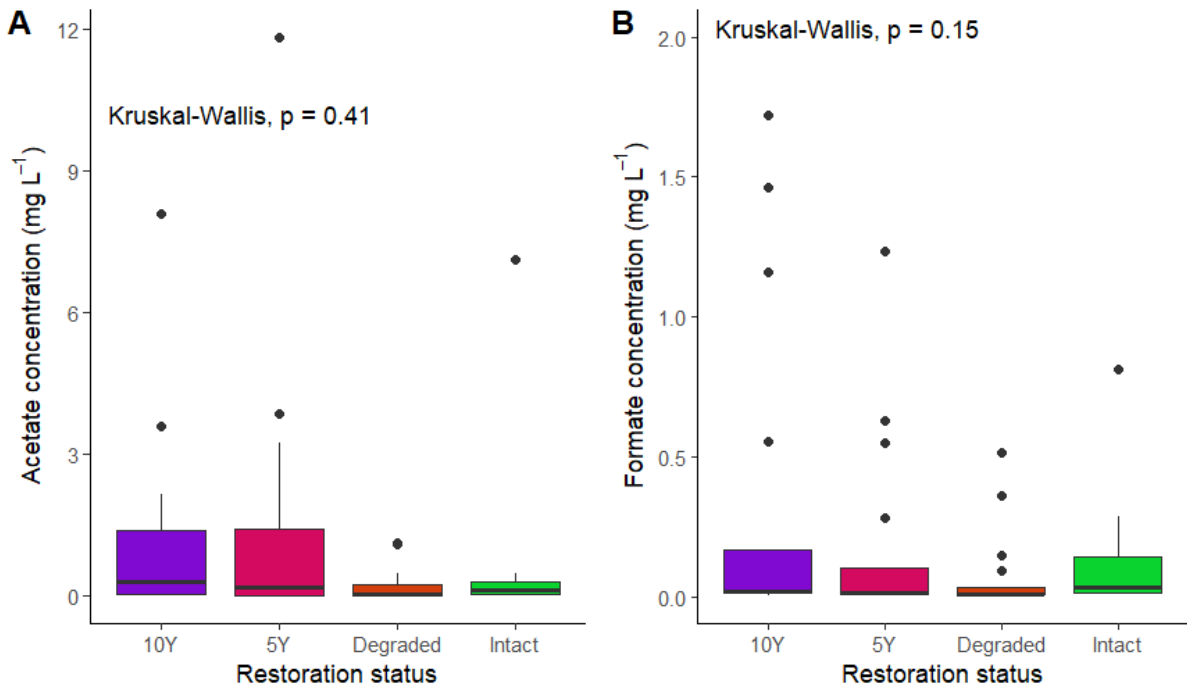


Figure 7.21 Acetate (**A**) and formate (**B**) concentration (mg L^{-1}) in pore water samples from degraded-restored peatland mesocosms from three blanket bog areas (Scotland, the Peak District, and Exmoor). Significance testing results shown.

7.3.6.1.3 Climatic regions

Acetate and formate concentrations varied significantly between climatic region (KW chi-squared = 13.664 and 21.149, df = 3, $p < 0.01$) with significant differences being shown in Table 7.6. Exmoor had the highest median concentration of acetate and formate of all four regions and the Peak District the lowest (Figure 7.22).

Table 7.5 Results of pairwise Wilcoxon statistical analysis of acetate (A) and formate (F) concentration (mg L^{-1}) for differences between the four regions of blanket bog. Significant differences are shown in **bold**.

	Exmoor		Peak District		Scotland	
	A	F	A	F	A	F
Peak District	**0.02**	**0.02**	-	-		
Scotland	**0.05**	0.36	0.54	0.102	-	-
Yorkshire	0.32	0.82	**0.04**	**<0.001**	0.143	**0.041**

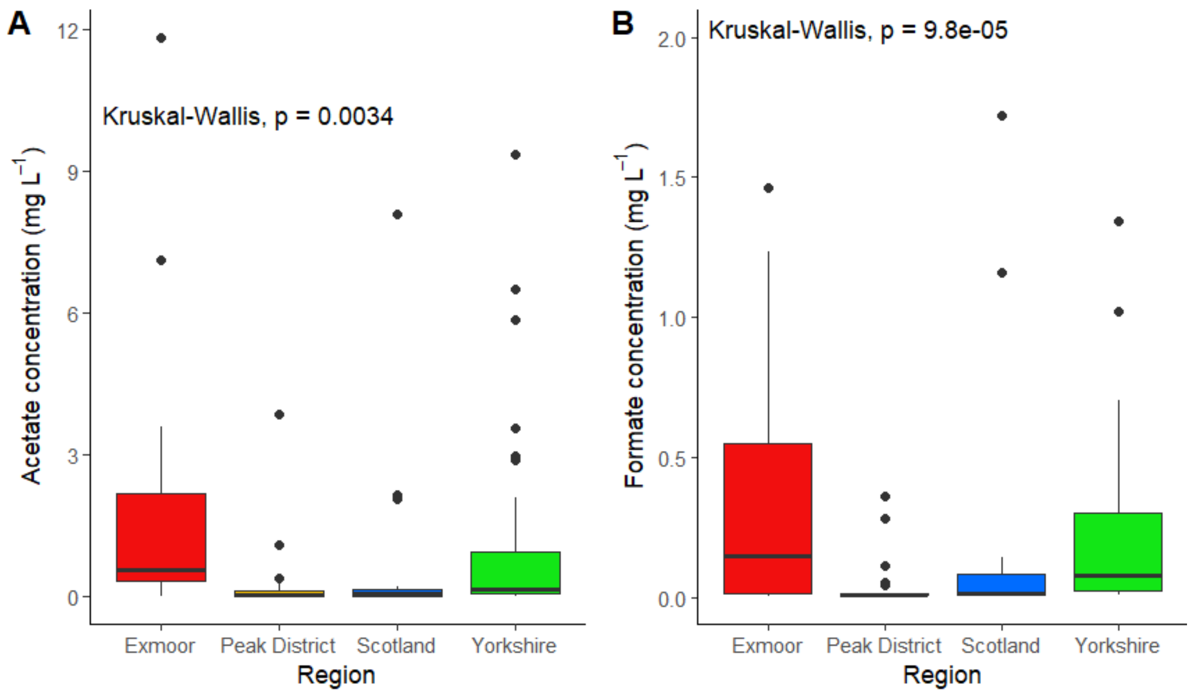


Figure 7.22 Acetate and formate concentration (mg L^{-1}) of peat mesocosm porewaters from four climatic regions (Exmoor, the Peak District, Yorkshire (of which one site situated in Lancashire), and Scotland). Kruskal Wallis statistical test result shown. Outliers shown.

7.3.6.1.4 Vegetation and acetate and formate concentrations

Samples taken from cores originating from Exmoor had the highest median acetate and formate concentrations, and these cores were dominated by *Molinia* grass, unlike cores from the other regions. It was therefore hypothesised that *Molinia* coverage (or perhaps more broadly grass cover) would be linked with higher HAA precursor concentration. However, Mantel analysis (Vegan R package, Oksanen *et al*., (2023)) indicated that neither geographical location or vegetation were significant drivers of differences in acetate and formate concentration (Mantel statistic; r = -0.009, p = 0.55 and r = 0.017, p = 0.37 respectively). % grass coverage was significantly positively correlated with acetate concentration (Pearson correlation coefficient = 0.26, p = 0.01) whilst formate concentration was significantly positively correlated with % grass and brash coverage (Pearson correlation coefficient = 0.22 and 0.26, p = 0.02 and p = 0.01, respectively).

7.3.6.2 Fourier Transform Infrared Spectroscopy (FTIR) and organic matter quality

FTIR scanning was performed on samples which had undergone coagulation as a preliminary analysis to help determine the nature of DOC present in peat porewater. All samples produced poorly defined spectra (Figure 7.23) but in all samples, four main peaks (Table 7.7) were identified. Due to low selectivity however, these correspond to several chemical groups.

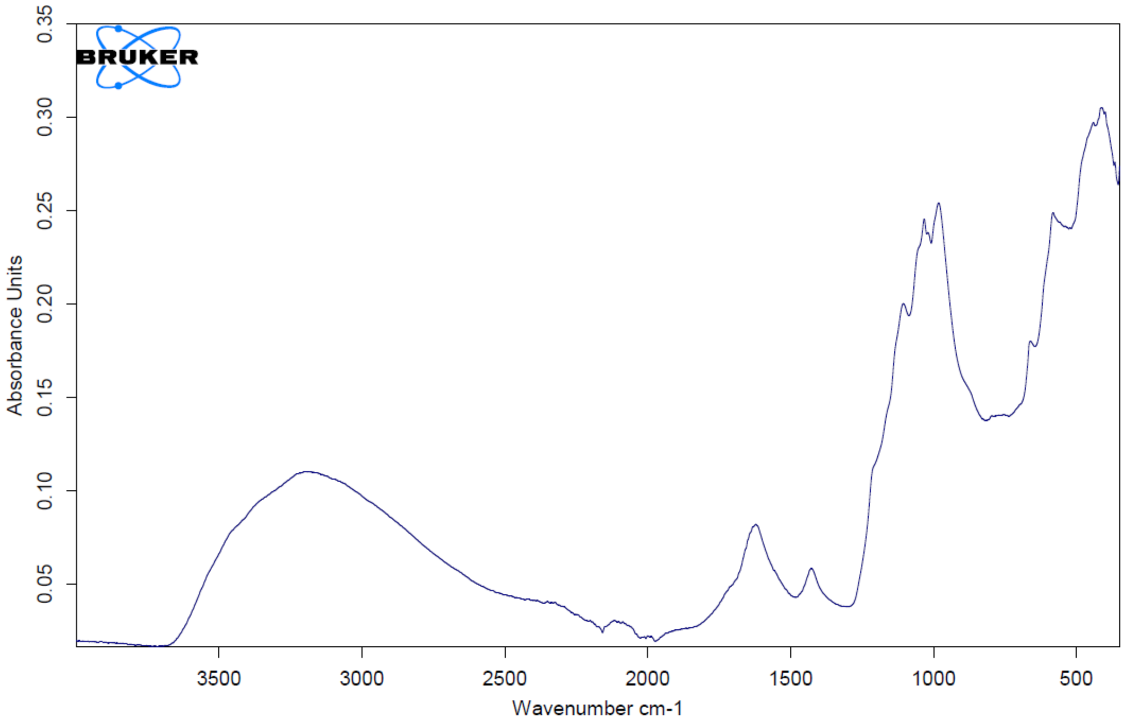


Figure 7.23 Example of a Fourier transform infra-red (FTIR) absorbance spectra obtained on the coagulant residue following the coagulation of DOC in mesocosm porewater using iron (III) sulphate. Sample analysed was from a Peak District (5-year post restoration) mesocosm core collected in July 2019.

Table 7.6 Wavelength range of four peaks identified during Fourier transform infra-red scanning between 4000-350 cm^{-1} for scanned samples. Table adapted from Artz *et al* (2017).

Wavelength range (cm^{-1})	Characterisation	Reference
3665 - 2177	Cellulose Fats, waxes and lipids	Cocozza *et al* (2003)
1825 - 1486	Carboxylic acids Lignin Proteinaceous origin	Cocozza *et al* (2003) Niemeyer *et al* (1992)
1486 - 1278	Humic acids Lignin	Parker (1971) Niemeyer *et al* (1992)
1278 - 883	Polysaccharides Cellulose Long chained alkanes	(Zaccheo *et al*., 2002)

7.4 Discussion

Results presented in this chapter provided some insight into the formation of DBP of waters under different vegetation communities because of management regime, restoration status, and climate. TCM formation following chlorination was considered in the context of overlying vegetation community composition along with the removal of DBP precursors via coagulation. Methods of DBP formation prediction were considered. Catchment management was considered as an alternative to traditional end-of-pipe treatment currently employed in the UK to both lower treatment costs and chemical demands.

7.4.1 Trihalomethanes prior to coagulation

In the UK, DBPs are heavily regulated and in potable water sources, the sum of THM_4 concentrations (as shown in Figure 2.7), must not exceed 100 µg L^{-1} (Liang and Singer, 2003). In peatland-draining catchments, recent and projected increases in DOC loads in raw waters (Evans *et al*., 2005; Xu *et al*., 2020b) will continue to be problematic to WT (Edzwald, 1993; Ferretto *et al*., 2021a). THM and HAA concentrations are known to vary according to precursor concentrations, with higher DOC concentration in raw waters corresponding to higher concentrations of DBPs, as shown in this study (Figure 7.2, Section 7.3.1) and within the wider literature (e.g. Liang and Singer, 2003).

TCM is found to be the dominant THM_4 formed following chlorination within the literature (Marais *et al*., 2019; O'Driscoll *et al*., 2018; Padhi *et al*., 2019), and in this study, TCM was the only THM_4 detected. It was anticipated that bromodichloromethane, dibromochloromethane, and bromomethane would be found at lower concentrations than TCM, given that in ombrotrophic peatlands, rainwater is the primary source of bromine. Bromine concentrations in rainwater is generally around 15 µg L^{-1} (Neal *et al*., 2007), which is reflected in low soil porewater concentrations of around 53-126 µg L^{-1} (Biester *et al*., 2006). However, at the time of writing and to the author's knowledge, UK focussed studies on peatland porewater halogen concentrations are non-existent. The presence of bromine in a water may affect DBP speciation (Liang & Singer, 2003), as formation of brominated DBPs occurs through the same mechanistic pathways as chlorinated DBPs, e.g. through electrophilic substitution (Reaction 2a in Table 7.8) and/or chlorine substitution (Reaction 2b in Table 7.8) (Langsa *et al*., 2017) (Table 7.8). However, as brominated THMs were not detected, it is likely that concentrations were below the GC-MS limit of detection (as seen in Marais *et al* (2019)), or due to the volatile nature of the compounds in question, evaporation from the water samples occurred prior to analysis. This therefore means that in peatland draining waters, brominated THMs may not be a significant risk.

Table 7.7 Reaction equations for the formation of brominated trihalomethanes during chlorination with sodium hypochlorite. OM refers to organic matter.

Equation	Reaction	Rate coefficient	Reference
1	$HOCl^- + Br^- \rightarrow HOBr + Cl^-$	k = 1.55 M^{-1} s^{-1}	Kumar & Margerum, 1987
2a	HOBr- + OM-Cl → OM-Br + HOCl-	*NA*	Langsa *et al*., 2017
2b	HOBr- + OM-Cl → OM-Cl-Br + H_2O		

This study found TCM production significantly correlated with DOC concentration, with higher DOC loads producing higher concentrations of TCM (Figure 7.2) which given the large range of DOC concentrations reported in this study, likely gives rise to the large range in TCM concentrations. This has also been demonstrated elsewhere in the literature (Singer & Chang, 1989; Valdivia-Garcia *et al*., 2019a), which was expected given that a higher DOC concentration represents a higher precursor load. Higher DOC concentration represents a challenge for DWT due to a higher coagulant demand (Edzwald, 1993). Where DOC concentrations > 4 mg L^{-1}, maintaining a THM concentration below the regulatory threshold of 100 µg L^{-1} for a contact time of 2-3 days (notably shorter than the standard contact time of 7 days in UK WTWs) with chlorine would be difficult (Ferretto *et al*., 2021b). It has been suggested that where DOC concentration > 4 mg L^{-1}, WTWs will likely be required to implement additional treatments, representing additional costs and treatment times (EPA, 2010; Ritson *et al.*, 2014). Considering this, managing peatlands in such a way which limits DOC production and dissolution is preferable, given that is widely known that peatlands are a significant source of OM in water courses elsewhere in catchments (Sepp *et al.*, 2019).

Table 7.8 Trichloromethane (TCM) concentrations (µg L^{-1}) reported in the literature in waters from various sources.

Measure	Notes	Reference
TCM concentration (µg L^{-1})		
of 1251.3 ± 1094 µg L^{-1}.	Mean and standard deviation of trichloromethane concentrations of mesocosm porewaters. Water sampled using 0.60 µm rhizon samplers and analysed in days following sample collection.	This study
81.01	Mean trichloromethane concentration of drinking water treatment plant water following coagulation from the US.	Chen and Westerhoff (2010)
243.70	Mean trichloromethane concentration of river waters from the US.	Chen and Westerhoff (2010)
TCM formation potential (µg^{-1} DOC mg L^{-1})		
279 ± 289	Mean and standard deviation of TCM formation potential of mesocosm porewaters.	This study
121.87	Mean THM_4 concentration of untreated water.	Golea *et al* (2017)

TCM concentrations were higher than those presented within the reviewed literature (Table 7.9), not only in peatland waters, but than those from various sources. This was expected firstly because coagulation had not taken place (Liang and Singer, 2003), and secondly, because water was taken directly from soil, degradation had not occurred to a degree expected of OM following movement through the catchment (i.e., Crapart *et al.*, 2021; Hansen *et al.*, 2016). This meant waters had a higher load of low molecular weight, high hydrophilicity compounds with poor removal efficiencies (Chu *et al.*, 2011) compared to waters typically entering WTWs. pH, contact time, and disinfection scenario were consistent with conditions in WTWs, and the chlorination method was provided by Yorkshire Water. Other factors known to affect TCM concentration include pH of solution undergoing chlorination, contact time, disinfection scenario, whether coagulation had been undertaken prior to chlorination and the potential for biodegradation of OM present in the water being treated (Liang & Singer, 2003).

7.4.1.1 Seasonality and trihalomethane concentration pre-coagulation

Seasonal differences were seen in pre-coagulation TCM concentrations, suggesting that temperature and water table depth (and thus soil moisture in the upper soil layers) influence TCM formation. Air temperature was also shown to be a significant driver in GLM modelling (Table 7.4). This is likely attributed to an increase in precursor availability. The decline in water table depth which accompanies a rise in temperatures increases peatland DOC export, likely due to increased plant and microbial productivity (Waddington *et al*., 2008). In addition, a rise in water table depths during periods of increased precipitation (with subsequent higher flow) and lower temperatures also likely alters DOC production (Wickland & Neff, 2008). Therefore, managing peatland vegetation with the aim of maintaining high water tables is suggested to be beneficial to WQ more broadly, and in the reduction of DBPFP of a water.

C storage in peatlands is thought to be partly regulated by the enzyme phenol oxidase (Freeman, Evans, *et al*., 2001). Phenol oxidase is shown to be constrained in cool, waterlogged conditions, but in summer months where temperatures are raised and water tables lower, phenol oxidase activity is enhanced (Freeman, Evans, *et al*., 2001). This leads to an increase in DOC production and subsequently, according to this work, TCM concentration post-chlorination. Increased temperatures and drought events because of climate change will cause a decline in average water table depth in peatlands (Ma *et al*., 2022), leading to increased DOC load in waters (Ferretto *et al*., 2021a; Gough *et al*., 2016) upon rewetting (Clark *et al*., 2005). A modelling study indicated that an average increase of 1.8°C will result in an increase of THM production in WTWs by 39% (Valdivia-Garcia *et al*., 2019a). In the forementioned study, no evidence was found for seasonal changes in DOC quality driving seasonal changes in THM concentration, and Golea *et al* (2017) concluded that variation in THM production in WTWs can be attributed to changes in the concentration of reactive OM rather than differences in OM quality.

TCM concentration was significantly lower in samples collected in April 2020 which is likely to be a result of a significantly lower water table depth (Figure 7.1) and thus soil moisture due to the limited access during this period (due to Covid-19 restrictions) to allow water level adjustments. An introduction of oxygen to the previously anoxic parts of the peat column leads to an increase in decomposition, and associated decline in DBP precursor material. Whilst this may be beneficial in the short-term, higher DOC concentrations may accompany rewetting due to flushing of the soil (Fenner and Freeman, 2011)(, thus increasing DBP precursor loads in draining waters.

7.4.1.2 Vegetation and trihalomethane concentration pre-coagulation

Vegetation influences the production and release of DOC (Awad *et al*., 2016) as it affects chemistry of soil water (Kuhry *et al*., 1993), physical peat soil properties (McNamara *et al*., 2008), biological agents within the peat (Artz *et al*., 2008), and the quantity and quality of plant and litter inputs (Moore and Dalva, 2001; Wickland *et al*., 2007). In peatland ecosystems, vegetation represents a significant OM input (Ritson *et al*., 2016). Radiocarbon studies indicate that surface water DOC is comprised mostly of fresh material, with likely origins in decaying litter and upper soil horizons (Palmer *et al*., 2001; Tipping *et al*., 2010). It is therefore proposed that vegetation management represents a radical alternative to traditional end-of-pipe treatment (Ritson *et al*., 2016) and could reduce DOC production/losses from peat soils. This would reduce a water's chemical demand and therefore the financial cost of drinking water treatment (Armstrong *et al*., 2012).

Cores dominated by *Molinia* grass had had the lowest concentration of all vegetation groups. This was expected given that DOC concentration was lowest in these cores. As previously shown, precursor concentration is the most significant factor in TCM formation in this study. *Molinia* grass has extensive root systems which can extend to depths of > 80 cm and responds well to water-logged conditions through aerenchyma (Taylor *et al*., 2001). The extensive root system causes water-table drawdown, increasing soil aeration and thus releasing exudates. These typically comprise of short chained compounds which are preferably utilised by microbiota. Therefore, in this experiment, OM was likely utilised by soil biota prior to sampling and chlorination.

It is widely reported within the literature that humic-like compounds are readily removed during coagulation, whereas the removal of proteinaceous DOC is more problematic (Ritson *et al*., 2016). Vegetation management for the reduction of DBPFP may include encouraging *Sphagnum* propagation and regeneration at the expense of more shrubby vegetation such as *C. vulgaris* (Campeau and Rochefort, 1996). Establishment of *Sphagnum* has been shown to increase soil moisture due to a higher water holding capacity (Antala *et al*., 2022; Malmer *et al*., 2003) which inhibits OM decomposition (Abbott *et al*., 2013). However, this would also depend upon peat composition and microbial communities (Laiho, 2006). The establishment of *Sphagnum* may also inhibit *C. vulgaris* overgrowth due to wetter soil conditions (Armstrong *et al*., 2012) and increased nutrient competition (Maimer *et al*., 1994), reducing the input of labile OM into peat soils. Whilst *Sphagnum* dominated cores did not exhibit significantly lower TCM production compared to other vegetation groups, concentration were lower than in *C. vulgaris* dominated cores. Thus, an effective management strategy may be to actively spread *Sphagnum* to encourage re-establishment and raise water tables at the possible expense of shrubby vegetation (Armstrong *et al*., 2012; Campeau & Rochefort, 1996). This may suppress the production of DOC, and thus limiting DBP precursor production.

7.4.1.3 Trichloromethane formation potential

The TCMFP of a water is dependent upon the composition of the DOC as precursor material, with hydrophobic components exhibiting around two times the TCMFP compared to hydrophilic counterparts (Chang *et al*., 2001). Hydrophobic (i.e., phenolic) fractions have been reported to produce more THMs and HAAs than other organic fractions (Kitis *et al*., 2004) and therefore, waters with a higher UV_{abs} – specifically UV_{254} and $SUVA_{254}$ - were predicted to have a higher TCMFP (Ghernaout, 2020). However, the correlation between UV_{254} and TCMFP was not significant (Table 7.3) suggesting that other factors in addition to OM composition are important in the formation of TCM in blanket bog porewaters. As with $SUVA_{254}$ (as outlined in Chapters 4,5, and 6), there were no significant differences between management regime, restoration status or climatic region in TCMFP. This supports the conclusion that the driving factor behind differences in TCM concentration post-chlorination are due to differences in DOC concentration, rather than differences in OM composition in blanket bog soils.

7.4.2 Haloacetic acids

HAA analysis was undertaken alongside THM analysis, but HAAs were not detected using the analytical methods available. Typically, DBPs are analysed using a GC-ECD, as it is a selective detector which is highly sensitive to electron reacting compounds containing halogens (Heng and Shellie, 2023). However, a GC-ECD was not available, so a GC-MS was used. The HAA extraction method provided by Yorkshire Water (Section 7.2.4) was used. However, HAA concentration likely was below the detection limit for the GC-MS (or the compounds evaporated before analysis). Steps were taken to improve the method, including detailed in Section 7.2.4. Comparison with DOC concentration and subsequent HAA formation reported in the literature suggested that HAAs would be formed at a concentration above the limit of detection (Table 7.10), and thus, it was concluded that the extraction method was unsuitable for the porewater samples, or it was not completed with sufficient efficiency.

Table 7.9 Dissolved organic carbon (DOC; mg L^{-1}) and haloacetic acid (HAA; µg L^{-1}) concentrations of waters reported in the literature. Formation potential refers to the concentration of HAAs formed per mg DOC. HAA_5 refers to the 5 most commonly formed HAA following chlorination.

Dissolved organic carbon concentration	HAA concentration	Notes	Reference
6.30 mg L^{-1}	-		This study
4.48 mg L^{-1}	290 µg L^{-1} C^{-1}	Mean DOC concentration HAA_5 formation potential	Kanokkantapong *et al* (2006)
7.74 mg L^{-1}	154.27 µg L^{-1} C^{-1}	Mean DOC concentration and HAA_5 formation potential	Golea *et al* (2017)

There are several mechanisms by which HAAs are formed, with hydrophobic (i.e., amino acids, sugars, and polysaccharides) and hydrophilic (i.e., cellulose) bases reported as being the most significant precursors. However, the mechanisms leading to the formation of HAAs in watercourses is likely to be location specific, and thus this should not be assumed to apply to all waters entering WTWs (Kanokkantapong *et al*., 2006). Similarly to THM, HAA concentration is reported as being significantly correlated to DOC concentration in raw (untreated) waters (Table 7.11) so in this study, it could be assumed that waters with a higher TCMFP will likely also produce more HAAs following chlorination.

Table 7.10 Regression analysis between dissolved organic carbon (DOC; mg L^{-1}) and haloacetic acid (HAA, µg L^{-1}) concentrations reported within the literature from different source waters.

R^2	Notes	Reference
0.96	Raw waters entering Bangkhen WTW, Thailand.	Kanokkantapong *et al* (2006)
0.74-0.79	Study presents range of R^2 for HAA formation potential with UV , hydrophobic fraction, and DOC concentration. Untreated waters taken from WTWs in Scotland, UK.	Golea *et al* (2017)

7.4.3 DOC removal efficiency

The procedure for coagulation and coagulant removal was found in US EPA 'Enhanced Coagulation and Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual' (1999). However initially, the OM did not coagulate in any sample. It was assumed that this was because DOC concentration was higher than waters which typically undergo coagulation, and thus the concentration of $FeSO_4$ in the coagulant solution was increased from 1 to 5 mg L^{-1}. A higher coagulant dose increases anion production, thus enhancing removal efficiency (Qian *et al*., 2019). Samples were then left for two weeks rather than the suggested ~0.5 hours (Environment Protection Agency, 1999), as coagulation did not occur despite stirring until this prescribed time. In addition, mean DOC removal efficiency was lower than reported by Ritson *et al.* (2016) (Table 7.12). It is suspected that this was likely due to the nature of compounds present in the water. Raw waters entering DWTPs has passed through the catchment and/or been stored in reservoirs where smaller, less recalcitrant (i.e. hydrophilic) molecules (which are known to resist coagulation) are utilised by microbes and undergo degradation. This therefore could represent a challenge for water utility companies where, because of drought, water has not been left for sufficient time in reservoirs due to low water supply. Thus, in such times, coagulation demand (and therefore dose) and coagulation time is likely to increase.

Table 7.11 Comparison with dissolved organic carbon (DOC; mg L^{-1}) removal efficiency (%) reported in this work and by Ritson *et al*. (2016).

Removal efficiency (%)	Notes	Reference
46.07 ± 24.62	Mean (± standard deviation) DOC removal from peat porewaters.	This study
83.4 ± 0.4 – 34.1 ± 0.4	Mean (± 1 std error) DOC removal originating from peat soils and 4 vegetation types. Peat soil had the highest mean % removal and *C.vulgaris* had the lowest.	Ritson *et al* (2016)

UV_{abs} of samples following coagulation was not measured due to the addition of iron as the coagulant. There are conflicting reports within the literature (for example, Asmala *et al*., 2012; Logozzo *et al*., 2022; Maloney *et al*., 2005; Weishaar *et al*., 2003) regarding the absorbance of iron (particularly Fe (III)) and the over-estimation of DOC absorbance. Some studies report that iron significantly contributes to UV-vis absorbance (Maloney *et al*., 2005) whilst others state that iron concentrations which are typical of surface waters have a negligible contribution to UV-vis absorbance of a water (Asmala *et al*., 2012; Weishaar *et al*., 2003). In such cases, it is recommended that an absorbance curve be plotted for iron concentration and absorbance and sample absorbance corrected accordingly. However, due to project time constraints, this was not possible. In addition, given that iron sulphate was added at a concentration of 5 mg L^{-1} (which is higher than the typical concentration in UK blanket bog (Burn, 2021), it was concluded that UV-vis absorbance of coagulated waters would not be representative of remaining DOC following coagulation.

DOC removal via coagulation had a mean % removal of 46.1 ± 24.6 %, which is lower than typical removal of raw waters within WTWs (Table 7.13). As previously detailed, as samples were taken directly from peat soils, the mechanisms which utilise and transform DOC within the catchment have not influenced DOC concentration nor OM characterisation. Thus, DOC is composed of a higher-than-normal portion of hydrophilic, non-UV absorbing compounds. Poor removal of hydrophilic OM components through coagulation is widely reported within the literature (Sadrnourmohamadi *et al*., 2013), and thus removal efficiency is lower than what would be expected during the treatment of drinking water. However, the patterns obtained are relevant to WT.

Table 7.12 % Dissolved organic carbon removal efficiency (%) reported by Ritson *et al* (2016) from peatland vegetation sources.

Vegetation group	% removal efficiency	Notes	Reference
C. vulgaris	43.22 ± 27.46	Dominant vegetation on cores – data from comparison of porewater DOC concentration pre- and post-coagulation.	This study
	34.10 ± 0.40	Plant litter	Ritson *et al* (2016)
Molinia grass	33.35 ± 21.72	As above	This study
	40.70 ± 0.60	As above	Ritson *et al* (2016)
Sphagnum spp.	47.01 ± 22.94	As above	This study
	64.1 ± 0.40	As above	Ritson *et al* (2016)

Cores which were dominated by *Sphagnum* had the highest mean % removal efficiency (47 ± 23 %) whilst cores dominated by *Molinia* had the lowest (33.3 ± 21.7 %). In a study by Ritson *et al* (2016), *Sphagnum* litter is reported as having a higher % removal efficiency than other peatland vegetation (Table 7.14). *Sphagnum* has been shown to produce labile DOC (Ritson *et al*., 2016), with a ^{13}C CPMAS NMR study showing a significantly lower signal intensity in the alkyl and aromatic-C ranges, suggesting a lower contribution of lipids and lignin/tannins respectively compared to *C. vulgaris* (Certini *et al*., 2014). The transformation of this labile OM through *in situ* microbial and chemical processes results in a lower portion of DOC dominated by highly aromatic fractions, which may be considered a positive from a water treatment perspective. This is because *Sphagnum*-DOC is likely to be mineralised while passing through the catchment, producing aromatic DOC which is amenable to removal via coagulation and flocculation (Matilainen *et al*., 2010; Ritson *et al*., 2016). Therefore, from a WT perspective, moving towards *Sphagnum* dominated bog may be preferential.

Proteinaceous DOC is more difficult to remove from drinking water than hydrophobic components (Qian *et al*., 2019; Ritson *et al*., 2016). The encroachment of vascular plants into *Sphagnum*-dominated bogs introduces DOC sources which are poorly removed by coagulation, and therefore may require alternative, more costly, treatment processes (Ritson *et al*., 2016) such as coagulation-UV/H_2O_2 oxidation (Qian *et al*., 2019). In *Molinia*-dominated systems, DOC mobility has been reported to be higher than in open-*Sphagnum* dominated systems, which has been attributed to increased rates of OM decomposition due to aeration of the soil (Meade, 2015). There are reports within the literature that in *Molinia*-dominated peat soils, there are low concentrations of DOC. This is in despite of a high rate of decomposition (Meade, 2015) and aeration deep into the soil column due to deep penetrating, aerenchyma roots (Loach, 1968). Therefore, as in this study, by sampling close to the soil surface (~15 cm), root exudates which are contributing to the soil DOC pool may not be detected (Meade, 2015). Furthermore, Certini *et al*. (2015) found that peat soils under *Molinia* had a significantly lower hydrophobicity index compared to *C. vulgaris*, indicating that a greater proportion of the DOC under *Molinia* is problematic for coagulation treatment processes. Ritson *et al*. (2017) also found that peat soils which had been exposed to oxygen produced DOC which was less amenable to coagulation and flocculation treatment methods. This is potentially significant in areas where vascular plant encroachment onto blanket bog is occurring or predicted to occur due to climate change induced drying.

The relatively low DOC % removal efficiency reported in this study is also significant considering predictions of increased drought events due to climate change (Jenkins *et al*., 2009). DOC exports are expected to increase (Ritson *et al*., 2017; Tang *et al*., 2013) along with hydrophobic OM fractions (Clark *et al*., 2012; Watts *et al*., 2001) in raw waters entering WTWs and DBPs formed following chlorination (Valdivia-Garcia *et al*., 2019). Waters typically spend 8 weeks within reservoirs (Jenny Banks, Yorkshire Water, *per comms*, 2023) which allows for processes such as biodegradation (Liu *et al*., 2021; Ni *et al*., 2022), photodegradation (Moran *et al*., 2000), and mineralisation (Dordoni *et al*., 2022) to occur. Preferential degradation of hydrophilic OM occurs (Liu *et al*., 2021) – as demonstrated by a ^{13}C CPMAS NMR study which indicated that soil derived OM had a significant increase in the alkyl-C contribution, along with a concomitant decrease in O-alkyl-C, which was attributed to a preferential biodegradation of carbohydrates over other OM groups (Baldock *et al*., 1992). This results in a dominance of aromatic (i.e., more recalcitrant) fractions within OM due to preferential degradation of hydrophilic OM (Liu *et al*., 2021). With increased pressure on water resources because of more frequent drought events (Cook, 2016) and a subsequent decline in peatland soil moisture and deeper water tables (Clark *et al*., 2012), DOC concentration and composition (due to aeration of the normally saturated peat soil column (Certini *et al*., 2015)) are likely to change. This will alter coagulant and chlorination demand during WT (Edzwald, 1993). In peatland soils, typically much of the peat profile is under saturated conditions (Holden *et al*., 2011) and therefore, a decline in water table depth because of increased temperatures and decreased precipitation is likely to increase pressure on WTWs and treatment processes due to higher precursor loading following rewetting (Clark *et al*., 2012).

However, it is important to note that maximising DOC removal during DWT does not necessarily assure the lowest THM formation (Sadrnourmohamadi *et al*., 2013) – coagulants which effectively remove the DOC fractions which contain the most DBP precursors successfully lower the DBPFP (Sadrnourmohamadi & Gorczyca, 2015b). Within this study (as discussed in more detail in Section 7.3.4), the concentration of TCM following coagulation was significantly lower compared to prior to coagulation. Therefore, in peatland draining waters, due to composition of OM, coagulation effectively removed a significant portion of DBP precursors.

7.4.4 TCM formation following coagulation

Coagulation is known to significantly reduce the DBPFP of a water, as has been demonstrated in laboratory and modelling studies (Chen & Westerhoff, 2010) and was shown in this study (Figure 7.11). Whilst the TCM concentrations following coagulation were significantly lower compared to pre-coagulation, concentrations still exceeded the UK regulatory threshold of 100 $\mu g\ L^{-1}$ (EC, 2020). Whilst as previously discussed, DOC and TCM concentrations in the waters studied were higher as they were taken directly from peat soils, this finding is significant given the increasing frequency of drought events and the shorter residence times waters have in reservoirs prior to being treated for domestic use. This is especially significant during storm events, whereby soil water storage is low and rapid saturation excess overland flow is generated. This can lead to soil erosion and increased OM loading in draining waters (Shuttleworth *et al*., 2019)

No differences were observed between waters from the various management regimes, restoration status', or climatic region in TCM formed following coagulation, meaning the differences observed prior to coagulation can be attributed to a higher presence of precursors (and thus OM) amenable to coagulation. Given that prior to coagulation the correlation between TCM and DOC concentration was significant, but no longer significant post-coagulation, it is suggested that the majority of TCM precursors were removed during coagulation.

7.4.5 Organic matter quality and characterisation

7.4.5.1 Acetate and Formate

Acetate and formate concentrations were significantly higher in samples from Exmoor cores (Figure 7.22) and were significantly positively correlated with % grass coverage. Acetate and formate are hydrophilic compounds, and thus not amenable to coagulation and do not absorb within the UV_{254}-UV_{400} typically used within the water industry to characterise DOC. Therefore, in waters draining from grass dominated catchments such as in Exmoor, SUVA cannot be used as a predictor for THM formation, indicating that SUVA does not capture reactive sites on OM moieties responsible for DPBs in such waters (Ates *et al*., 2007)(. There was no significant difference in acetate and formate concentrations between management regimes which was expected given there was no difference in UV_{254} or $SUVA_{254}$ in samples from grouse-managed cores. Concentrations of porewaters from burnt cores had the highest median formate and acetate concentrations, whilst mown cores had the lowest. Acetate is the dominant metabolic end-product following the degradation of *Sphagnum*-derived polysaccharides by *Acidobacteriota* (Duddleston *et al*., 2002; St. James *et al*., 2021). It is also important to note that acetate has been reported to be the primary organic terminal product of anaerobic decomposition in peat soil (Duddleston *et al*., 2002), and therefore increased concentrations may lead to increased CO_2 production with peat soils.

7.4.5.2 HPLC analysis for fulvic & humic acids

Porewaters were analysed for fulvic and humic acids using HPLC, but the chromatograms were too complex to resolve any peaks. HPLC has been widely used to characterise OM matter within waters (e.g. Her *et al*., 2002), but to elude OM molecular weight and structure in peat porewaters, substantial sample preparation would be required. Unfortunately, due to project time constraints, this was not possible. The characterisation of humic and fulvic acids would be an important step in furthering understanding of DBP precursors, and the characterisation of OM within peat soil water.

7.4.5.3 FTIR

Prior to the Covid-19 pandemic, FTIR was planned to be used as an initial screening tool to provide a 'fingerprint' of the characterisation of DOC in the peat mesocosm porewaters. However, due to time constraints, it was undertaken much later than initially planned. It is hoped however, that it may be useful as a preliminary step towards characterising DOC alongside techniques such as NMR. Initially, 20 samples were prepared for FTIR scanning, but only 13 were left with sufficient residue following drying to be analysed. Peaks were poorly defined for scans of all samples which is likely due to the heterogeneous, complex nature of organic matter within peatland systems. Four main peaks were identified, and peak areas were found to vary between samples, however the sample set was too small to make any meaningful comparison between climatic region, management and/or RS. It may also be possible that due to the addition of iron (III) sulphate as a coagulant, residual iron within the DOC residue may affect absorbance at certain wavelengths. Rouchon *et al* (2012) used FTIR to characterise a large set of iron sulphates in fossil materials with samples showing well defined absorbance peaks at 1300 cm^{-1} – 100 cm^{-1}. Therefore, in any quantification study (if analysing chemically coagulated DOC), absorbance by the coagulant must be taken into account, especially as in this study, the volume of coagulant added was in accordance with DOC concentration. During future analysis, it is recommended that coagulant also be scanned to be used as a potential 'blank' sample, against which sample spectra can be corrected against.

7.4.6 Predicting disinfectant-by production formation

7.4.6.1 UV absorbance

UV absorbance is widely accepted to be a proxy for OM characteristics, namely the phenolic character of OM (Edzwald *et al*., 1985). Given it is understood that chlorine attacks the phenolic components of OM within solution (Kim *et al*., 2002), it can be assumed that UV absorbance could be used to infer DBPFP of a raw water (Beauchamp *et al*., 2019b). Some studies have found significant correlations between UV absorbance and DBP production and formation potential, but it has been noted that these cannot be applied to all raw waters (Beauchamp *et al*., 2019a). This is due to OM being a mixture of both hydrophobic and hydrophilic OM components, originating from allochthonous and autochthonous sources (Bond, Goslan, *et al*., 2012). For example, the relationship between SUVA and the formation of total THM is dependent on the activated aromatic structures which are the major components of natural organic matter (NOM). In high SUVA waters, high chlorine reactivity resulted in the formation of more THMs than in low SUVA level waters (Özdemir *et al*., 2013). As phenolic compounds are amenable to coagulation and are thus more readily removed from waters, wavelengths which are useful proxies for TCM formation can also be used as % DOC removal predictors.

Wavelengths which are commonly used to predict DOC concentration were significant predictors of DBPFP, with hazen producing a model of the lowest RMSE (Table 7.3). This was expected given the significant correlation between DOC concentration and TCM concentration prior to coagulation, and aromatic fractions largely contribute to colour and DBP formation in raw waters. However, whilst activated aromatic compounds are well known DBP precursors, less acknowledged but nonetheless significant compounds are amino acids, carbohydrates, and *β*-dicarbonyls which do not absorb strongly within the UV region (Korshin *et al*., 1996). Therefore, an effective predictive method or strategy must consider both hydrophilic and hydrophobic OM components (Bond, *et al*., 2012). As shown in Chapters 5 and 6, samples from Exmoor blanket bog have comparatively low DOC concentrations and UV absorbance, but high acetate and formate concentrations which are not amenable to coagulation and thus potentially contribute to the pool of OM important in DBP formation. Therefore, to account for the high DFPFP of low-UV absorbing chemical groups, a dual-wavelength model is a more effective tool in predicting the DBPFP of a raw water (Carter *et al*., 2012; Tipping *et al*., 2009)(and is a suggestion for further work.

7.4.6.2 Differential UV absorbance

Relationships between chlorination conditions (e.g., pH, temperature, chlorine, and NOM concentration) and the formation of DBPs is highly complex and thus difficult to ascertain and predict (Özdemir *et al*., 2013). Substantial work (e.g., Ates *et al*., 2007; Beauchamp *et al*., 2019; Beauchamp *et al*., 2019b; Korshin *et al*., 1996; Özdemir *et al*., 2013; Roccaro & Vagliasindi, 2009) has been undertaken in attempt to identify a useful surrogate for DBPFP to predict and/or monitor the formation of DBPs, of which for this work, UV absorbance and SUVA are most relevant. Correlations between total THMs and total HAAs, and ΔA_{272} have been reported (Roccaro & Vagliasindi, 2009) and thus may be reflective of DBPFP, and an indication of whether the OM present in waters is rich in active chromophores or dominated by groups characteristic of low absorbances (Table 7.14). These findings were reflected in this study as seen in Section 7.3.3. Waters within and draining from peat catchments exhibit a high contribution of hydrophobic compounds forming the OM pool (demonstrated by high SUVA and hazen values widely reported within the literature and within this study), which absorb within the 254 nm – 400 nm range (as seen in Peacock *et al*., 2014). It is understood that chlorine attacks the bonds absorbing in this range, thus causing a decline in absorbance during the chlorination process (Beauchamp *et al*., 2019a). Thus, waters with a high SUVA (>4) were expected to have a higher ΔUV_{abs}.

ΔUV_{272} 2 hours post-chlorination was significantly correlated with TCM concentrations (Figure 7.9) as also reported in the literature (Özdemir *et al*., 2013; Roccaro and Vagliasindi, 2009). However, absorbance post-chlorination does not produce a more accurate predictive model compared to absorbance at 272 nm pre-chlorination, and thus measuring raw water absorbance at 272 nm is considered a more effective proxy for TCM formation given there is no need for sample preparation and analysis.

Differential UV broad spectrum analysis showed a peak in absorbance for 270 nm – 290 nm (Figure 7.9). Within the literature, a peak in absorbance is reported for 270 nm – 290 nm (Beauchamp *et al*., 2019). Whilst absorbance does not increase at this wavelength range, the rate in absorbance decrease lowers. This was also observed by Beauchamp, Dorea, Beaulieu, *et al* (2019) who attributed this to phenolic structures contributing to the formation of DBPs. The longer the time since chlorination, the greater the decrease in ΔUV_{abs} for all wavelengths tested, indicating the destruction of UV-absorbing sites. It may also be inferred that the concentration of THMs produced in chlorine-treated waters increases with increasing time and pH (Özdemir *et al*., 2013).

However, the usefulness of ΔUV_{abs} is contested, as the fitting parameters between ΔUV_{abs} and DBP formation varies between water sources and within the same water depending upon time of year (Beauchamp *et al*., 2019). In some cases, rapid formation of THM and HAAs have been reported, so differential UV_{abs} may be a good predictor for final THM and HAA concentrations post-chlorination (Liang & Singer, 2003). Whilst differential absorbance may be a useful parameter for monitoring the destruction of OM during chlorination, it has been reported that it is not a useful indicator of the DBPFP of a water. In a study by Ates *et al* (2007), no significant correlations between total THM and HAA formation and ΔUV_{abs} were reported, suggesting DBP formation is independent of the destruction of UV absorbing sites within OM.

Table 7.13 Summary of differential ultraviolet (UV) absorbance experiments within the literature. R^2 represents the coefficient of determination between change in absorbance at key wavelengths.

Wavelength	R^2	Notes	Reference
UV_{272}	> 0.96	Quantified with linear equations. Lake water from Tukey.	Özdemir *et al* (2013)
	0.80 – 0.94	Water treatment works inlet and outlet waters in the Ancipa reservoir, Italy. Reaction times 10 minutes – 72 hours.	Roccaro & Vagliasindi, (2009)
UV_{260} – UV_{275}	> 0.80	Linear regression for trihalomethanes. Raw waters collected from lakes and rivers in the US.	Beauchamp *et al* (2019)

7.4.7 Water treatment and blanket bog management

No significant differences were observed for TCM concentration between grouse-moor management regime. Uncut cores had the highest median TCM concentration but given there was a positive correlation between DOC and TCM concentrations (Figure 7.2), this finding was expected. TCMFP also did not differ between management regime, which was again expected given SUVA did not differ between management regime (Section 4.3.5.6) and thus, the chemical groups comprising the DOC were assumed to be largely similar between treatments. *C. vulgaris* has been reported to produce more DOM in the laboratory (Ritson *et al*., 2016; Grayson *et al*., 2012)) and at plot scale (Armstrong *et al*., 2012) compared to other peatland vegetation groups. This was also reflected in this study given *C. vulgaris* was significantly associated with uncut cores (Table 3.4). In the absence of management (leading to tall *C. vulgaris* plants), there is less input of plant litter and labile material into soil and thus a comparatively lower turnover of OM. This results in an accumulation of recalcitrant material within the peat, leading to an increase in porewater DOC concentration. This accumulation means there is a higher concentration of precursor material, and thus a higher potential for TCM to be produced upon chlorination. Thus, as land management impacts peatland vegetation coverage (Noble *et al*., 2018), any differences in DOC concentration which appear to be due to land management (i.e., Glaves *et al*., 2013; Ramchunder *et al*., 2013) may be attributed to subsequent changes in vegetation post-management (Armstrong *et al*., 2012). However, hydrophobic compounds which have been associated with a dominance of *C. vulgaris* are readily removed via traditional coagulation methods (Ritson *et al*., 2016), so waters draining from such areas may not pose a significant risk in terms of DBP production post-coagulation. However, Ritson *et al* (2016) found DOC from *Molinia* had a higher % removal via coagulation compared to *C. vulgaris*, and therefore management which encourages *Molinia* growth may be preferable in the context of water treatment.

Studies examining the impact of moorland burning and DBP formation were not found within the literature, but other studies have investigated the impacts of fire more generally, and the subsequent impacts upon DBPs at WTWs. For example, Wang *et al*., (2016) investigated temporal variation in DBP precursors following a wildlife in California. They found that in periods following a precipitation event which proceeded the burn, a decrease in DOC concentration was accompanied with an increase in dissolved organic matter (DOM) aromaticity, leading to an increase in reactivity to form THMs and HAAs. Whilst it is important to note that the nature of wildfire is very different from prescribed peatland burning, this increase in DOM aromaticity (inferred by increases in UV_{abs} at wavelengths as described in Section 4.3.5.6), has been reported in other studies, and may not be captured in this work due to the time elapsed since burning which in this study, was 11 years (see Brown *et al.,* (2015)).

As there were no significant differences between UV_{abs} at key wavelengths, it was hypothesised that DOC removal efficiency would not differ between management regimes. As uncut cores showed significantly higher DOC concentration overall in comparison to burnt and mown cores, it was suspected uncut cores would show a higher DOC removal efficiency, but this was not the case. However, as the sample size was relatively small, it would be valuable to repeat this analysis.

7.4.8 Water treatment and blanket bog restoration

Overall, there were no significant differences between restoration status and TCM concentration; however, TCM produced in samples from intact cores were significantly lower compared to degraded cores. This is likely due to the drawdown in water table depth which accompanies degradation – particularly following drainage (Holden *et al*., 2004) - and subsequent oxygenation of upper soil layers. As there was no significant difference in median DOC concentration for intact and degraded samples, the composition of the DOC is likely to contribute to this difference. Median hazen was higher in degraded samples compared with intact samples, but this difference was not significant. $SUVA_{254}$ showed a similar trend. Degraded cores therefore may have a larger contribution of hydrophilic, non-UV absorbing compounds to the OM pool resulting from water table drawdown. This could be attributed to the breakdown of the phenol-oxidase mechanisms and the subsequent degradation of more recalcitrant, UV-absorbing phenolic components of OM (Freeman, *et al*., 2001). It is also important to note that restored samples exhibited lower TCM concentrations compared to degraded cores, providing evidence that in terms of water treatment, restoration is beneficial.

There were no significant differences in DOC removal efficiency between RS. However, samples from intact cores showed a higher median % DOC removal than degraded and restored cores. Peatland soils which undergo degradation commonly experience water table drawdown and thus aeration of soil layers (Gough *et al*., 2016). This oxygenation of previously saturated and anoxic soils leads to increased rates of decomposition of OM (Fenner and Freeman, 2011b), thus preventing the accumulation of recalcitrant compounds seen in intact, functioning peatland soils. This effect is long-lasting, and thus, the impact on WQ may be a legacy effect which is seen even 10Y post-restoration.

7.4.9 Water treatment and blanket bog climatic region

TCM concentrations were shown to differ significantly between region, with Exmoor showing lower TCM concentrations compared to the other three regions. However, GLM modelling indicates that coverage of grass and *C. vulgaris* were significant drivers, suggesting that vegetation coverage is a significant driver in the formation of TCM following chlorination. The Exmoor core samples had significantly higher formate and acetate concentrations compared to other regions. This is again, likely linked to *Molinia* coverage, which causes water table drawdown and a significant input of leaf litter and labile material due to root exudates (Meade, 2015). However, with DOC increasing with climate warming (Fenner *et al*., 2021), there may be an increase in recalcitrant compounds within the DOC pool due to a more rapid turnover of more labile OM by microorganisms.

% DOC removal was shown to vary significantly with climatic region. Exmoor showed the lowest median % removal whilst Yorkshire had the highest. The sampling site in Exmoor is the warmest of the three regions and receives the lowest mean annual rainfall (Table 6.1). However, as previously discussed, it is dominated by *Molinia* grass which is known to cause water table drawdown due to a high root mass which leads to subsequent soil aeration. It is likely that because of these processes, rates of decomposition are increased, leading to a decline in the accumulation of recalcitrant OM which is readily removed during coagulation. However, Mantel analysis indicated that vegetation was overall not a significant driver of % DOC removal, so environmental conditions also need to be considered as an explanatory factor (e.g., temperature as a constraint on plant and soil microbial activity and water table depth limiting oxygen availability).

7.4.10 Significance for drinking water treatment

It is important to note that the samples analysed in this study were not directly representative of those entering WTWs. The concentration and composition of DOC within raw waters entering WTWs reflect the abiotic and biotic processes (such as microbially mediated decomposition, sedimentation, and natural flocculation) which OM is subjected to as it passes through the catchment. In addition to blanket bog being a significant source of DOC, OM is also generated within lakes and reservoirs (which are becoming an increasingly important store of water as climate and land pressures increase water demand) through photosynthetic processes and thus, the DOC concentration and composition at this point represent the sum of the removal and generation processes (Williamson *et al*., 2022). However, this work highlights that there is potential to manage plant community composition to ameliorate observed rising DOC concentrations (Armstrong *et al*., 2012) through blanket bog management (shown in Chapter 4) and restoration (Chapter 5). Although present-day vegetation may be different from which the underlying SOM originated (Chambers *et al*, 1999; Hjelle *et al*., 2010), many studies have demonstrated that the most active part of SOM is the youngest (e.g., Leavitt *et al*., 1996; Trumborfe 2000; Chiti *et al*., 2009) and thus, current management and restoration practices are significant both now and for the future.

Future work is needed to understand how DOC in peatland draining catchments is transformed throughout the catchment and how processes such as mineralisation, UV degradation, and microbial transformation impacts DOC and POC composition and the potential significance of these changes in the context of drinking water treatment. Moreover, in the context of drought, porewaters may be more representative of waters entering WTWs when pressures on water resources held in reservoirs increases, reducing reservoir residence times.

7.5 Conclusion

This study has shown that the most significant determining factor in the DBPFP of a water is DOC concentration. In peatland draining waters (which are typically of high colour), a large portion of DOC comprises of large, complex compounds such as fulvic and humic acids, which are amenable to coagulation and thus do not pose a risk in the context of DBP formation.

In the context of blanket bog vegetation management, results indicated that there is no 'preferable' management regime if reducing DBP formation in WTWs was the aim. However, considering that DOC is a precursor to DBP, managing vegetation by burning or mowing reduces this load, and may lead to a reduction in coagulant demand of waters. Furthermore, this study has indicated that the encroachment of vascular plants (in this case *Molinia*) may lead to an increase of compounds less amenable to coagulation, thus representing a threat to DW quality and treatment. Restoration and management should be undertaken with the aim of maintaining high (i.e., near to surface) water tables to encourage longer-term C sequestration along with a DOC load dominated by more recalcitrant compounds.

Hypothesis 1 was proven to be incorrect. Whilst DOC concentration was significantly positively correlated with TCM formation due to an increased TCM precursor loading, there were no significant differences in TCM formation in blanket bog management regime despite a significant difference in DOC concentration between uncut, and burnt and mown cores. This was linked to no significant differences between TCMFP. Hypothesis 2 was also proven to be incorrect. Degraded cores had a significantly higher TCM prior to coagulation despite there being no significant difference between DOC concentration, but there was no significant difference in TCMFP between any restoration status. Samples from restored cores had lower TCM concentrations and % DOC removal rates following coagulation compared to intact and degraded cores, indicating that the progression from a degraded to intact state occurs over a longer time scale than is measured in this study. Hypothesis 3 was proven to be correct. UV_{254} and UV_{400} were significantly correlated with TCM concentration (prior to coagulation) indicating that absorbance at these wavelengths can be a useful predictor of the TCMFP.

The results presented here have significance for water storage in times of drought, which are predicted to increase in frequency with climate warming projections. More labile DOC (and POC) is preferentially utilised by microbes, but in times of drought, water may be stored in reservoirs for shorter periods. This reduces the time for these processes to occur, leading to an increase in shorter chained OM fractions in waters entering WTWs. As these compounds are less amenable to coagulation, they represent a significant source of DBP precursors, and thus represent a mechanism by which the production of DBP can increase with climate warming. Blanket bogs are a significant source of DBP precursors, and this work indicates that vegetation management and restoration can reduce coagulant demand and improve DOC composition to make it more amenable to coagulation and removal. As discussed in the previous chapters, the effects of restoration and vegetation management vary between sites, and therefore optimal management in the context of improving water quality is site dependent.

8 Summary

8.1 Chapter outline

Bringing together the discussion and conclusion sections in Chapters 4, 5, 6, and 7, this chapter summarises this thesis in its entirety and discusses how the results have contributed to answering the overarching research questions:

1) Does heather management benefit water quality and C fluxes, and can alternative mowing management be used to overcome any effects associated with prescribed burning?
2) Does blanket bog restoration benefit water quality and C fluxes?
3) How will climate change impact blanket bog ecosystem service provisioning?

The findings of this project are discussed in the context of these questions, and the implications for management and restoration are explored. Findings which extend or challenge current knowledge and understanding are considered, along with project limitations. General conclusions and recommendations for blanket bog management and restoration, and further research are outlined.

8.2 Overview of methodology and studied systems

This thesis analysed data obtained from field mesocosm sites and peat core mesocosms which were situated in York. Peat cores were obtained in February 2019, along with data pertaining to environmental conditions and geographical information. Mesocosm core water table depth was maintained (as far as possible) to mimic in-field conditions and were periodically sampled for porewater samples using rhizon samplers, and GHG fluxes measured (as reported in Chapters 4, 5, and 6). Vegetation surveys were undertaken annually in September. Mesocosm access was restricted in the first half of 2020 due to Covid-19 restrictions, which also hindered laboratory analysis. Porewater samples were analysed for water quality parameters: dissolved organic carbon (DOC) concentration, pH, conductivity, and UV absorbance (as reported in Chapters 4, 5, and 6). Where sample volume was sufficient, samples were later analysed for disinfectant by-products (DBPs) and ease of DOC removal via coagulation (as reported in Chapter 7).

8.3 Impacts of blanket bog vegetation management on ecosystem service provisioning

Work undertaken to investigate the effects of blanket bog vegetation management upon water quality and GHG fluxes was part of a larger, long term (10-years), robust Before-After-Control-Impact (BACI) study (Heinemeyer *et al*., 2023). Whilst annual average air temperature was higher and precipitation lower at the mesocosm site compared to in the field, comparisons between results obtained from the mesocosm cores and field measurements show similar trends (Section 4.2.1). Whilst it could be criticised that the environmental conditions at the mesocosm sites differ from those in the field – therefore affecting the parameters investigated – this difference affected all mesocosms similarly. This allowed exploration of a causal link between management and restoration and observed differences in water quality and greenhouse gas (GHG) fluxes. To the author's knowledge, this is the first such study to compare intact and fully replicated blanket bog mesocosms to findings from a BACI field experiment on burning, mowing, and no heather management.

Management (prescribed burning and alternative mowing) was shown to improve water quality through the reduction of DOC loading and colours in waters (Section 4.3.5). Reports of the effects of burning upon DOC are conflicting (e.g., (Brown *et al*., 2014; Worrall *et al*., 2007) and remain a contentious issue (Worrall *et al*., 2013a). DOC concentration was higher in unmanaged cores, attributed to a lower turnover of organic matter (OM) in the underlying peat soil and accumulation of more recalcitrant OM (Section 4.3.5.1). This was further supported by higher UV absorbance at key wavelengths (254 nm = UV_{254} and 400 nm= UV_{400}). Specific UV absorbance ($SUVA_{254}$ and $SUVA_{400}$) did not significantly differ between management regimes indicating that the differences in UV absorbance were due to differences in DOC concentration rather than composition (Section 4.3.5.6). High SUVA values (> 4) indicated that DOC was dominated by hydrophobic and recalcitrant compounds (Section 4.3.5.6.1).

Uncut cores were significantly associated with *C. vulgaris* (Section 4.3.3), which was an expected finding given that vegetation management is undertaken to promote *C. vulgaris* regrowth. Uncut cores were also significantly associated with *Sphagnum*, indicating that management impacts non-target species (Noble *et al*., 2018a). Mown cores were significantly associated with sedge, which has been linked with higher CH_4 fluxes due to aerenchyma tissues allowing CH_4 to by-pass oxidation in the soil oxic-zone (Akhtar *et al*., 2021; Bhullar *et al*., 2013). Sedge coverage was positively correlated with CH_4 flux (Section 4.3.6.4). *Sphagnum* coverage was highest at Mossdale which was the wettest (highest annual precipitation) site. DOC concentration and UV_{254} absorbance were lower in porewaters from Mossdale compared to the other sites, indicating that a higher *Sphagnum* coverage may benefit water quality (Section 4.4.5). This may be offset however by the higher CH_4 fluxes measured in Mossdale cores.

Mesocosm soil respiration (SR) was higher than measurements reported for the field sites (Heinemeyer *et al*., 2023), and uncut plots had the highest median flux and mown the lowest in both the mesocosms and the field (Section 4.5.6.1). Net ecosystem exchange (NEE) did not differ between management regime but did differ between site, indicating that environmental conditions and specific site conditions exert a larger influence on GHG fluxes than management (Section 4.3.6.2). Ecosystem respiration (R_{eco}) showed the same differences. Whilst disentangling the effects of vegetation and environmental conditions upon GHG fluxes is difficult, this indicates that the optimal management regime is site-dependent, and therefore more long-term measurements would be beneficial to project vegetation recovery trajectory and associated impacts on water quality and GHG flux.

In summary, differences water quality variables and GHG fluxes between management regimes at the same site indicated that the most suitable management regime should be determined by site-specific aspects (i.e., climate and topography). Management should also be chosen based upon the overarching management aim (i.e., to increase C uptake thus reducing GHG flux, or to improve water quality), as it has been shown, that in some cases, the conditions which lead to an improvement in the provisioning of one ecosystem service can cause a decline in another (Section 4.3.5 and Section 4.3.6).

8.4 Impacts of blanket bog restoration on ecosystem service provisioning

This study investigated the effects of restoration upon blanket bog water quality and GHG fluxes by comparing mesocosm cores from degraded – 5 years and 10 years post restoration – intact sites from three regions of blanket bog in the UK (Section 5.2). Sites in Exmoor and Scotland had undergone drainage with associated water table drawdown, whereas at sites in the Peak District, in addition to drainage, prolonged historical atmospheric pollution deposition had led to elevated soil metal concentrations (Rosenburgh, 2015).

Results showed that intact cores were significantly associated with *Sphagnum* species which is attributed to higher water tables (Section 5.3.1). DOC concentrations were significantly higher in intact cores (along with UV_{254} absorbance) indicating a more recalcitrant OM pool which is beneficial in long-term soil C storage (Section 5.3.3). Degraded cores had significantly higher exposed bare peat compared to other restoration statuses (Section 5.3.1). The Peak District bare cores had 100 % bare peat coverage and did not recover over the course of this study. This study also indicated that restoration success is likely site specific. Cores from Exmoor did not differ between restoration status in water quality or GHG flux – unlike other sites – which is likely due to high *Molinia* coverage on all cores (Section 5.3.1 and Section 3.2.4.3). This leads to water table drawdown and represents a significant input on labile OM into the soil, which can lead to increased decomposition rates and CO_2 soil flux.

It is acknowledged that the same restoration methods do not achieve the same outcome at all sites (Parry *et al*., 2014). To improve understanding of the impacts of restoration upon ecosystem service delivery in peatland ecosystems, more BACI studies are needed with regular and long-term monitoring (i.e., > 10 years). Whilst restoration is a crucial step in halting peatland degradation, it is imperative that the potential outcomes are well understood by both practitioners and policymakers, and on what timescales these outcomes are expected to come to fruition (Gatis *et al*., 2023). This thesis has demonstrated that mesocosms represent a useful tool in comparing the response of different vegetation types under similar climatic conditions to restoration practices, and any associated changes in water quality and GHG fluxes.

8.5 Impacts of climate upon blanket bog ecosystem service provisioning

Using blanket bog mesocosm cores collected from four distinct 'climatic' regions in the UK, this work explored the implications of climate upon blanket bog ecosystem service provisioning. Whilst it must be acknowledged that the peat cores were removed from these climatic regions, 'memory effect' due to microbial community composition and abundance will have implications for water quality and GHG fluxes (Canarini *et al*., 2021).

This work showed that temperature exerts a significant control over GHG fluxes and water quality (Section 6.3.4 and Section 6.3.5). Water quality and GHG fluxes differed significantly on a seasonal basis, with higher concentrations and fluxes in warmer conditions due to lower soil moisture and deeper water tables and elevated concentrations following warmer conditions are due to rewetting and soil flushing. With higher predicted temperatures predicted due to climate change (specifically temperature extremes), and alterations to precipitation regimes (Watts *et al*., 2015), this has significant implications for future water quality in blanket bog draining catchments.

The warmest site included in this study was Exmoor, which was characterised by a higher cover of *Molinia* and had the lowest DOC concentrations on a seasonal basis of all sites. Whilst this may be beneficial for water quality, lower SUVA indicates the water is less amenable to coagulation, and therefore represents a significant source of DBP precursor material (Section 6.3.4). Whilst more labile, hydrophilic compounds give waters a lower SUVA, this material is preferentially utilised by soil microbes and is more readily degraded when waters move through the catchment. However, as frequency of drought increases, this may represent a significant source of DBP precursors, particularly when water is removed from reservoirs without sufficient time for microbial and UV OM degradation. Therefore, restoration and management should be undertaken with the aim of shifting a *Molinia* (or more broadly vascular plants) dominated vegetation community to a more desirable state – i.e., *Sphagnum* dominated, whereby water tables are raised, and decomposition suppressed. The coolest site (the Peak District) had the lowest GHG fluxes and DOC concentrations. The vegetation community in this region was more characteristic of blanket bog – higher coverage of *C. vulgaris* and *Sphagnum* – and coupled with lower temperatures, likely led to reduced decomposition rates and OM turnover.

8.6 Blanket bogs and drinking water treatment

This study used mesocosm porewaters collected from four regions of UK blanket bog under various management regimes and restoration status to investigate the formation of DBPs in blanket bog draining waters upon chlorination. DOC concentration was the most significant determining factor in the DBP formation potential (DBPFP) of a water (Section 7.4.1), which as shown in previous chapters, is influenced by overlying vegetation community composition. In this study, porewaters were generally of high SUVA (> 4), indicating that a large portion of DOC is comprised of large, complex compounds such as fulvic and humic acids (Section 4.3.5 and Section 5.3.3). These are amenable to coagulation and thus do not pose a significant risk in the context of DBP formation. Waters from the Exmoor cores had a lower median SUVA (indicative of a higher hydrophilic OM fraction) compared to the other sites, which is problematic in the context of DBP formation, as DOC is less readily removed with traditional coagulation methods.

In the context of blanket bog vegetation management for water quality, results indicated that there is no 'preferable' management regime if reducing DBP formation in drinking water treatment is the overarching aim. However, reducing DOC loading in waters by managing vegetation (either by burning or mowing, or restoration) may lead to a reduction in coagulant demand (Section 7.4.1). Furthermore, this study has indicated that the encroachment of vascular plants (in this case *Molinia*) may lead to an increase of compounds less amenable to coagulation (Section 7.3.4.4), which has implications on drinking quality and treatment efficiencies. Restoration and management should therefore be undertaken with the aim of maintaining high (i.e., near to surface) water tables to encourage longer-term C sequestration along with a DOC load dominated by more recalcitrant, colour-producing compounds.

It is important to note that the samples analysed in this study were not directly representative of those entering water treatment works. The concentration and composition of DOC within raw waters entering WTWs reflect catchment conditions and processes, and in these experiments, samples were taken directly from the mesocosm cores. However, this work highlights (in Chapter 4 and Chapter 5) that there is potential to manage plant community composition to ameliorate observed rising DOC concentrations (Armstrong *et al*., 2012). Although present-day vegetation may be different from which the underlying organic material originated (Chambers *et al*, 1999; Hjelle *et al*., 2010), the most active part of SOM is the youngest (e.g., Leavitt *et al*., 1996; Trumborfe 2000; Chiti *et al*., 2009). Therefore, present-day management and restoration practices are significant both now and for the future. In addition, it would be useful to repeat the analysis with additional samples with sufficient sample volumes to extract and analyse the same sample several times to obtain replicates. This was not done in this study due to sample volume available and financial constraints.

Future work is needed to understand how DOC in peatland draining catchments is transformed throughout the catchment. In the context of drought, porewaters may be more representative of waters entering WTWs when water availability is lower and demand for water held in reservoirs increases, reducing reservoir residence times. Therefore, these results may provide some insight into DBP formation under future projected climate conditions. Further characterisation of chemical groups forming DOC under different vegetation communities would be beneficial in developing more effective predictive methods of the disinfectant by-production formation potential of a raw water.

8.7 Conclusions and recommendations

Peatlands are a globally significant C store and, in the UK, a significant provider of ecosystem services (Reed *et al*., 2014). Protecting and managing and thus maximising the provisioning of these services whilst addressing the interests of various stakeholders has historically been challenging and remains so. Long-term and regular monitoring of UK blanket bog is required if we are to further understand the underpinning processes which regulate water quality and GHG fluxes. However, this comes with significant associated costs, both logistically and financially. Mesocosms offer an opportunity to bridge the gap between field and lab experiments, and in this study, meaningful comparisons were able to be made using a BACI approach.

Perhaps most importantly, this study has demonstrated that the impacts of management and success of restoration are site specific, and site conditions must be considered when considering *C. vulgaris* management and blanket bog restoration practices. In addition, longer-term monitoring is essential if understanding of the effects of said practices are to be further understood. It is recommended that further work be undertaken into characterising DOC components to determine which chemical groups are characteristic of overlying vegetation community composition. This could then be linked with UV-vis absorbance – a cost-effective analytical tool – and a more effective predictive method of DBPFP be developed. Long-term monitoring of water quality and GHG fluxes is important moving forwards, as current monitoring work is poorly funded or not undertaken for a sufficiently long period. This would enable better assessment of the trajectories of ecosystem service delivery, so we can respond with appropriate management and restoration practices to project blanket bog in the context of unprecedented anthropogenic driven climate change.

9 Appendices

Appendix 1. Example data table for carbon dioxide gas fluxes collected for calculation of net ecosystem exchange and ecosystem respiration. Data shown here is for cores from Exmoor.

File Name	Lin_Flux	Mean Tcham	Mean V1	Month	Year	Core
HE-NEE_050522_17	-3.84	26.27	1278	May	2022	E10Y1
HE-NEE_050522_17	0.52	27.53	886	May	2022	E10Y1
HE-NEE_050522_17	0.89	27.66	503	May	2022	E10Y1
HE-NEE_050522_17	4.53	26.43	0	May	2022	E10Y1
NEE_150621_17	-15.86	35.14	1452	June	2021	E10Y1
NEE_150621_17	-9.39	35.97	1026	June	2021	E10Y1
NEE_150621_17	7.65	35.73	233	June	2021	E10Y1
NEE_150621_17	15.15	33.48	0	June	2021	E10Y1
NEE_HE170122_17	-0.63	4.26	146	January	2022	E10Y1
NEE_HE170122_17	-0.28	4.15	46	January	2022	E10Y1
NEE_HE170122_17	1.01	3.74	0	January	2022	E10Y1
NEE_060521_17	-1.11	14.79	401	May	2021	E10Y1
NEE_060521_17	0.98	15	257	May	2021	E10Y1
NEE_060521_17	1.54	14.99	107	May	2021	E10Y1
NEE_060521_17	1.88	14.38	0	May	2021	E10Y1
NEE_HE101121_17	-2.85	15.02	180	November	2021	E10Y1
NEE_HE101121_17	2.43	15.13	44	November	2021	E10Y1
NEE_HE101121_17	2.72	14.84	0	November	2021	E10Y1
HE_NEE031219_PLOT17.81x	0.26	9.95	288.44	December	2019	E10Y1
HE_NEE031219_PLOT17.81x	0.9	10.1	46.90	December	2019	E10Y1
HE_NEE031219_PLOT17.81x	1.27	9.48	0.00	December	2019	E10Y1
HesEast_050220_NEE17.81x	-0.53	7.69	235.42	February	2020	E10Y1
HesEast_050220_NEE17.81x	-0.36	8.45	214.09	February	2020	E10Y1
HesEast_050220_NEE17.81x	0.58	7.93	0.00	February	2020	E10Y1
HEplot17NEE_010819.81x	-26.44	25.93	1632.7	August	2019	E10Y1
HEplot17NEE_010819.81x	-5.92	26.49	469.093	August	2019	E10Y1
HEplot17NEE_010819.81x	12.56	26.13	0	August	2019	E10Y1
HE_NEE_031022_17.81x	-3.84	16.54	135	October	2022	E10Y1
HE_NEE_031022_17.81x	-0.97	16.74	85	October	2022	E10Y1
HE_NEE_031022_17.81x	2.62	16.71	38	October	2022	E10Y1
HE_NEE_031022_17.81x	5.3	16.19	0	October	2022	E10Y1
HesEast17_210720	-20.83	24.08	470.14	July	2020	E10Y1
HesEast17_210720	0.65	24.26	80.00	July	2020	E10Y1
HesEast17_210720	10.63	23.43	0.00	July	2020	E10Y1
HesEastNEE17_151020	0.67	16.62	292.56	October	2020	E10Y1

HesEastNEE17_151020	4.07	16.59	154.96	October	2020	E10Y1
HesEastNEE17_151020	7.41	16.11	0.00	October	2020	E10Y1
HE_NEE233102019_plot17.81x	-23.4	16.67	1421.19	October	2019	E10Y1
HE_NEE233102019_plot17.81x	-7.24	18.85	341.52	October	2019	E10Y1
HE_NEE233102019_plot17.81x	3.58	18.52	0.00	October	2019	E10Y1
HE_NEE291019_PLOT17.81x	-4.43	14.18	615.67	October	2019	E10Y1
HE_NEE291019_PLOT17.81x	0.14	14.58	122.87	October	2019	E10Y1
HE_NEE291019_PLOT17.81x	0.71	13.98	0.00	October	2019	E10Y1
HE-NEE_050522_39	-4.55	27.84	1381	May	2022	E10Y2
HE-NEE_050522_39	1.78	30.73	1007	May	2022	E10Y2
HE-NEE_050522_39	5.6	31.68	505	May	2022	E10Y2
HE-NEE_050522_39	8.26	30.84	0	May	2022	E10Y2
NEE_150621_39	-6.98	31.19	1448	June	2021	E10Y2
NEE_150621_39	0.53	32.69	1118	June	2021	E10Y2
NEE_150621_39	8.17	33.37	328	June	2021	E10Y2
NEE_150621_39	15.88	32.2	0	June	2021	E10Y2
NEE_HE170122_39	0.02	6.38	283	January	2022	E10Y2
NEE_HE170122_39	0.19	6.52	81	January	2022	E10Y2
NEE_HE170122_39	0.35	5.74	0	January	2022	E10Y2
NEE_060521_39	-2.33	17.3	1283	May	2021	E10Y2
NEE_060521_39	-1.98	20.18	939	May	2021	E10Y2
NEE_060521_39	1.49	20.98	261	May	2021	E10Y2
NEE_060521_39	3.65	19.53	0	May	2021	E10Y2
NEE_HE101121_39	1.52	14.6	185	November	2021	E10Y2
NEE_HE101121_39	1.75	14.83	44	November	2021	E10Y2
NEE_HE101121_39	2.17	14.64	0	November	2021	E10Y2
HE_NEE031219_PLOT39.81x	-1.32	13.55	267.47	December	2019	E10Y2
HE_NEE031219_PLOT39.81x	0.69	14	19.02	December	2019	E10Y2
HE_NEE031219_PLOT39.81x	1.33	13.03	0.00	December	2019	E10Y2
HesEast_050220_NEE39.81x	-0.84	8.76	430.01	February	2020	E10Y2
HesEast_050220_NEE39.81x	-0.04	10	292.89	February	2020	E10Y2
HesEast_050220_NEE39.81x	0.77	9.84	0.00	February	2020	E10Y2
HEplot39NEE_010819.81x	-26.59	29.69	834.539	August	2019	E10Y2
HEplot39NEE_010819.81x	-8.17	29.86	535.622	August	2019	E10Y2
HEplot39NEE_010819.81x	11.57	29.84	0	August	2019	E10Y2
HE_NEE_031022_39.81x	-3.36	19.64	260	October	2022	E10Y2
HE_NEE_031022_39.81x	0.91	19.8	161	October	2022	E10Y2
HE_NEE_031022_39.81x	3.21	19.26	68	October	2022	E10Y2
HE_NEE_031022_39.81x	5.15	18.43	0	October	2022	E10Y2
HesEast39_210720	-22.23	25.98	1512.15	July	2020	E10Y2
HesEast39_210720	2.08	28.24	595.76	July	2020	E10Y2
HesEast39_210720	6.88	26.26	0.00	July	2020	E10Y2
HesEastNEE39b_151020	-3.73	15.4	361.05	October	2020	E10Y2
HesEastNEE39b_151020	-1.77	15.63	199.60	October	2020	E10Y2

HesEastNEE39b_151020	3.71	15.13	0.00	October	2020	E10Y2
HE_NEE233102019_plot39.81x	-5.17	14.43	314.31	October	2019	E10Y2
HE_NEE233102019_plot39.81x	-1.24	14.54	66.18	October	2019	E10Y2
HE_NEE233102019_plot39.81x	3.43	14.19	0.00	October	2019	E10Y2
HE_NEE291019_PLOT39.81x	-1.66	11.45	378.64	October	2019	E10Y2
HE_NEE291019_PLOT39.81x	1.16	11.73	111.56	October	2019	E10Y2
HE_NEE291019_PLOT39.81x	1.27	11.49	0.00	October	2019	E10Y2
HE-NEE_050522_61	-4.91	24.13	591	May	2022	E10Y3
HE-NEE_050522_61	1.1	24.76	397	May	2022	E10Y3
HE-NEE_050522_61	1.97	24.95	221	May	2022	E10Y3
HE-NEE_050522_61	6.89	24.45	0	May	2022	E10Y3
NEE_150621_61	-23.55	31.79	1646	June	2021	E10Y3
NEE_150621_61	-17.32	33.42	1244	June	2021	E10Y3
NEE_150621_61	1.55	34.05	473	June	2021	E10Y3
NEE_150621_61	9.41	32.77	0	June	2021	E10Y3
NEE_HE170122_61	-0.27	8.51	205	January	2022	E10Y3
NEE_HE170122_61	-0.05	8.34	53	January	2022	E10Y3
NEE_HE170122_61	0.19	7.77	0	January	2022	E10Y3
NEE_060521_61	-2.35	21.75	830	May	2021	E10Y3
NEE_060521_61	0.44	20.85	545	May	2021	E10Y3
NEE_060521_61	2.44	23.26	264	May	2021	E10Y3
NEE_060521_61	3.11	22.51	0	May	2021	E10Y3
NEE_HE101121_61	0.26	14.53	173	November	2021	E10Y3
NEE_HE101121_61	1.25	14.7	61	November	2021	E10Y3
NEE_HE101121_61	2.13	14.49	0	November	2021	E10Y3
HE_NEE031219_PLOT61.81x	-0.78	7.92	80.31	December	2019	E10Y3
HE_NEE031219_PLOT61.81x	-0.31	8	14.90	December	2019	E10Y3
HE_NEE031219_PLOT61.81x	0.52	7.77	0.00	December	2019	E10Y3
HesEast_050220_NEE61.81x	-0.64	10.95	241.74	February	2020	E10Y3
HesEast_050220_NEE61.81x	0.19	10.81	137.12	February	2020	E10Y3
HesEast_050220_NEE61.81x	0.66	10.4	0.00	February	2020	E10Y3
HEplot61NEE_010819.81x	-17.61	22.39	337.619	August	2019	E10Y3
HEplot61NEE_010819.81x	1.44	22.63	96.372	August	2019	E10Y3
HEplot61NEE_010819.81x	9.63	22.34	0	August	2019	E10Y3
HE_NEE_031022_61.81x	-4.09	17.61	193	October	2022	E10Y3
HE_NEE_031022_61.81x	-2.44	17.81	125	October	2022	E10Y3
HE_NEE_031022_61.81x	1.38	17.71	57	October	2022	E10Y3
HE_NEE_031022_61.81x	3.35	17.4	0	October	2022	E10Y3
HesEast61_210720	-17.18	20.88	443.57	July	2020	E10Y3
HesEast61_210720	2.59	21.1	108.51	July	2020	E10Y3
HesEast61_210720	5.88	20.52	0.00	July	2020	E10Y3
HesEastNEE61_151020	-3.25	17	340.66	October	2020	E10Y3
HesEastNEE61_151020	-1.85	17.44	260.10	October	2020	E10Y3
HesEastNEE61_151020	3.08	17.57	0.00	October	2020	E10Y3

HE_NEE233102019_plot61.81x	-2.66	18.01	685.82	October	2019	E10Y3
HE_NEE233102019_plot61.81x	0.81	18.49	75.22	October	2019	E10Y3
HE_NEE233102019_plot61.81x	2.11	17.87	0.00	October	2019	E10Y3
HE_NEE291019_PLOT61.81x	-0.41	10.91	120.73	October	2019	E10Y3
HE_NEE291019_PLOT61.81x	0.73	10.98	30.38	October	2019	E10Y3
HE_NEE291019_PLOT61.81x	1.09	10.84	0.00	October	2019	E10Y3

Appendix 2. Example vegetation survey data. Sites included are those discussed in Chapter 6. Vegetation coverage corrected for canopy and under canopy coverage. Values presented are % vegetation coverage.

Sample	Site	Management	Heather	Shrub	Herb	Sedge	*Molinia*	Other moss	Grass	Lichen	Bare	Brash	pel_lac	U luzula spp	Salez
SI1	Scotland	Intact	19.23	1.54	0.77	0.77	53.85	16.15	3.08	0.77	0.00	3.85	0.00	0.00	0.00
S10Y2	Scotland	10Y	3.23	25.81	0.00	22.58	44.52	0.65	0.00	1.29	0.00	1.94	0.00	0.00	0.00
SD1	Scotland	Degraded	4.81	0.00	0.00	4.81	0.00	0.00	0.00	0.00	85.58	4.81	0.00	0.00	0.00
S5Y3	Scotland	5Y	28.74	0.60	0.00	12.57	41.92	1.20	0.00	0.00	0.00	14.97	0.00	0.00	0.00
S5Y1	Scotland	5Y	33.33	0.00	0.00	5.71	9.52	0.00	36.19	0.95	0.00	14.29	0.00	0.00	0.00
S10Y3	Scotland	10Y	12.98	2.29	0.00	12.98	69.47	0.00	0.00	0.00	0.00	2.29	0.00	0.00	0.00
SI2	Scotland	Intact	12.50	0.00	0.00	4.17	66.67	0.00	0.00	0.83	0.00	15.83	0.00	0.00	0.00
S5Y2	Scotland	5Y	36.67	12.00	2.00	13.33	28.00	1.33	3.33	0.00	0.00	3.33	0.00	0.00	0.00
SD2	Scotland	Degraded	9.90	1.98	0.00	9.90	0.00	0.00	0.00	0.00	4.95	73.27	0.00	0.00	0.00
SI3	Scotland	Intact	19.86	0.00	0.68	8.90	48.63	0.00	0.68	0.00	0.00	21.23	0.00	0.00	0.00
SD3	Scotland	Degraded	19.01	0.00	0.00	17.61	0.00	0.00	0.00	59.86	1.41	2.11	0.00	0.00	0.00
S10Y1	Scotland	10Y	24.00	4.00	0.00	12.00	0.00	9.60	0.00	0.80	0.00	49.60	0.00	0.00	0.00
PI1	Peak District	Intact	0.00	0.86	0.00	80.17	0.00	10.34	0.00	0.00	0.00	8.62	0.00	0.00	0.00
PI3	Peak District	Intact	0.00	0.00	0.00	89.52	0.00	5.71	0.00	0.00	0.00	4.76	0.00	0.00	0.00
PD1	Peak District	Degraded	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00
PD3	Peak District	Degraded	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00
PD2	Peak District	Degraded	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100.00	0.00	0.00	0.00	0.00
P5Y3	Peak District	5Y	47.02	0.00	0.66	6.62	0.00	36.42	3.97	0.00	0.00	3.31	1.99	0.00	0.00

P5Y2	Peak District	5Y	29.41	0.00	0.00	15.29	0.00	50.00	0.59	0.00	0.00	4.71	0.00	0.00	0.00
PI2	Peak District	Intact	0.00	49.62	0.00	7.63	0.00	27.48	0.00	0.00	0.00	15.27	0.00	0.00	0.00
P10Y1	Peak District	10Y	0.00	0.00	0.00	27.62	0.00	53.33	10.48	0.00	0.00	8.57	0.00	0.00	0.00
P10Y2	Peak District	10Y	41.67	0.00	0.00	12.50	0.00	25.00	0.83	0.00	0.00	20.00	0.00	0.00	0.00
P10Y3	Peak District	10Y	35.90	0.00	0.00	34.19	0.00	11.97	1.71	0.00	0.00	16.24	0.00	0.00	0.00
P5Y1	Peak District	5Y	22.15	0.00	0.00	22.15	0.00	44.94	1.27	0.00	0.00	9.49	0.00	0.00	0.00
E5Y1	Exmoor	5Y	0.00	0.00	0.00	0.00	0.00	11.33	64.02	0.00	0.00	24.65	0.00	0.00	0.00
EI3	Exmoor	Intact	0.00	0.00	0.00	40.94	36.91	0.00	13.42	0.00	0.00	8.72	0.00	1.34	0.00
ED1	Exmoor	Degraded	12.50	0.00	0.63	0.00	50.00	0.00	18.75	0.00	0.00	18.13	0.00	0.00	0.00
ED2	Exmoor	Degraded	0.00	5.78	0.00	17.34	37.57	4.05	32.37	0.00	0.00	2.89	0.00	0.00	0.00
EI2	Exmoor	Intact	3.73	0.00	0.00	28.36	20.15	0.75	35.82	0.00	0.00	11.19	0.00	0.00	0.00
E10Y1	Exmoor	10Y	0.00	0.00	0.00	0.60	0.00	18.07	54.22	0.00	0.00	27.11	0.00	0.00	0.00
E10Y2	Exmoor	10Y	0.00	0.00	3.23	0.00	0.00	10.32	56.13	0.00	0.00	30.32	0.00	0.00	0.00
ED3	Exmoor	Degraded	0.00	0.00	0.00	58.33	5.00	9.17	20.83	0.00	0.00	6.67	0.00	0.00	0.00
E10Y3	Exmoor	10Y	0.00	0.00	0.00	0.00	0.00	0.00	59.35	0.00	1.94	38.71	0.00	0.00	0.00
E5Y3	Exmoor	5Y	0.00	0.00	0.00	0.00	0.00	15.00	67.86	0.00	4.29	12.86	0.00	0.00	0.00
E5Y2	Exmoor	5Y	0.00	0.00	0.00	0.55	0.00	10.50	51.93	0.00	0.55	36.46	0.00	0.00	0.00
EI1	Exmoor	Intact	0.81	0.00	8.94	28.43	36.56	0.89	4.06	0.00	0.00	20.31	0.00	0.00	0.00

Appendix 3. Samples analysed for trihalomethane concentrations following coagulation. Dissolved organic carbon concentration post coagulation shown. Chlorine was added at 5 mg L^{-1} 1 mg L^{-1} DOC. As samples were 50 mL, the volume of chlorine solution to be added was calculated as Cl mL = DOC * 5 / 20.

Sample number	Month	Year	Name	Site	Management	DOC post coag	Cl to be added
19	April	2021	SD2	Scotland	Degraded	1.38	0.34
59	November	2022	P10Y3	Peak District	10Y	1.61	0.40
57	November	2022	PD3	Peak District	Degraded	1.62	0.41
52	November	2022	NM4	Nidderdale	Mown	1.80	0.45
10	April	2021	NF3	Nidderdale	Burnt	1.88	0.47
20	April	2021	E10Y3	Exmoor	10Y	1.92	0.48
24	April	2021	S5Y1	Scotland	5Y	1.96	0.49
58	November	2022	SI3	Scotland	Intact	1.99	0.50
54	November	2022	P10Y1	Peak District	10Y	2.06	0.51
21	April	2021	NM4	Nidderdale	Mown	2.09	0.52
17	April	2021	S10Y2	Scotland	10Y	2.15	0.54
18	April	2021	P10Y2	Peak District	10Y	2.29	0.57
55	November	2022	WM4	Whitendale	Mown	2.40	0.60
47	November	2022	S10Y3	Scotland	10Y	2.46	0.62
37	November	2022	PD2	Peak District	Degraded	2.52	0.63
23	April	2021	S5Y2	Scotland	5Y	2.52	0.63
11	September	2020	MU1	Mossdale	Uncut	2.58	0.64
33	November	2022	ED2	Exmoor	Degraded	2.60	0.65
1	April	2021	P5Y2	Peak District	5Y	2.61	0.65
56	November	2022	MF3	Mossdale	Burnt	2.73	0.68
14	August	2019	SI2	Scotland	Intact	2.90	0.72
8	September	2020	NF4	Nidderdale	Burnt	2.96	0.74
3	January	2020	PD2	Peak District	Degraded	3.01	0.75
25	April	2021	P5Y3	Peak District	5Y	3.07	0.77
5	August	2019	P10Y1	Peak District	10Y	3.09	0.77
53	November	2022	MF2	Mossdale	Burnt	3.15	0.79
35	November	2022	ED1	Exmoor	Degraded	3.21	0.80
9	August	2019	PD3	Peak District	Degraded	3.21	0.80
22	April	2021	PI2	Peak District	Intact	3.33	0.83
46	November	2022	EI1	Exmoor	Intact	3.37	0.84
51	November	2022	S10Y1	Scotland	10Y	3.41	0.85
15	August	2019	WU3	Whitendale	Uncut	3.51	0.88
61	November	2022	NM1	Nidderdale	Mown	3.55	0.89

60	November	2022	WM3	Whitendale	Mown	3.64	0.91
38	November	2022	P10Y2	Peak District	10Y	3.74	0.94
48	November	2022	E10Y1	Exmoor	10Y	3.96	0.99
27	November	2022	S5Y2	Scotland	5Y	4.00	1.00
12	August	2019	SD2	Scotland	Degraded	4.00	1.00
42	November	2022	E5Y2	Exmoor	5Y	4.13	1.03
34	November	2022	NF4	Nidderdale	Burnt	4.20	1.05
40	November	2022	S10Y2	Scotland	10Y	4.29	1.07
28	November	2022	E10Y2	Exmoor	10Y	4.41	1.10
2	January	2020	PD3	Peak District	Degraded	4.53	1.13
39	November	2022	NF1	Nidderdale	Burnt	4.59	1.15
36	November	2022	MU3	Mossdale	Uncut	4.86	1.21
4	November	2022	WM1	Whitendale	Mown	4.86	1.22
44	November	2022	E5Y1	Exmoor	5Y	5.02	1.25
45	November	2022	WU4	Whitendale	Uncut	5.07	1.27
13	August	2019	E10Y3	Exmoor	10Y	5.07	1.27
32	November	2022	WM1	Whitendale	Mown	5.27	1.32
7	August	2019	P5Y3	Peak District	5Y	5.34	1.34
49	November	2022	MU2	Mossdale	Uncut	5.38	1.34
29	November	2022	WU1	Whitendale	Uncut	5.44	1.36
41	November	2022	MF4	Mossdale	Burnt	5.50	1.37
50	November	2022	WU3	Whitendale	Uncut	5.57	1.39
16	August	2019	MM4	Mossdale	Mown	5.66	1.42
26	November	2022	E5Y3	Exmoor	5Y	5.68	1.42
31	November	2022	EI2	Exmoor	Intact	5.98	1.50
43	November	2022	NF3	Nidderdale	Burnt	7.31	1.83
6	August	2019	WF1	Whitendale	Burnt	8.96	2.24

Appendix 4 Collection dates of mesocosm porewater samples. Collection times are approximate (within 2 hours) and refer to the time the sample tubes were set and collected.

Collection	Year	Month	Date collection tubes set	Approx. time collection tubes set	Samples collected	Approx. time samples collected
1	2019	July	30.07.2019	17:00	31.07.2019	08:00
2		October	28.10.2019	16:00	29.10.2019	10:00
3	2020	January	28.01.2020	15:00	29.01.2020	10:00
4		June	09.06.2020	17:00	10.06.2020	09:00
5		September	25.09.2020	17:00	26.09.2020	09:00
6	2021	February	20.02.2021	15:00	21.02.2021	11:00
7		April	28.04.2021	16:00	29.04.2021	10:00
8		August	10.08.2021	18:00	11.08.2021	09:00
9		November	25.11.2021	14:00	26.11.2021	11:00
10	2022	November	01.11.2022	14:00	02.11.2022	10:00

Appendix 5 Environmental conditions during: 1) 27 days prior and the day of (i.e. previous month), 2) 13 days prior and the day of (i.e. previous fortnight), 3) 6 days prior and the day of (i.e. previous week), and 4) day prior and day of mesocosm pore water collection (i.e. previous 48 h). Average air temperature, light level and precipitation was obtained from the on-site weather station, average soil temperature, and soil moisture readings were taken from in situ soil probes. Collection dates can be seen in Table 3.16.

Collection	Average air temperature (°C)				Average soil temperature -5 cm below peat surface (°C)				Light level Sum mol m^{-1} PAR2				Soil Moisture (%)				Precipitation (sum of, mm)			
	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
1	18.3	19.5	20.4	18.8	18.5	19.4	20.1	19.9	915.9	423.4	939.7	50.0	94.2	94.3	94.1	94.3	45.2	48.2	36.6	7.6
2	9.1	8.0	6.7	5.4	10.4	9.6	8.6	7.1	242.7	115.9	48.7	18.9	96.3	96.3	96.2	96.8	86.4	42.2	35.0	0.0
3	5.8	4.6	5.0	5.1	5.0	4.2	4.4	4.0	111.0	71.5	35.6	9.6	96.4	96.4	96.5	96.5	27.2	4.4	1.6	0.6
4	13.7	14.1	11.1	12.0	13.7	14.1	11.1	12.0	1116.8	621.3	187.1	65.1	71.2	60.0	63.6	67.0	25.2	22.0	22.0	0.2
5	13.8	14.0	12.4	9.1	14.5	14.6	13.8	12.0	606.3	296.4	129.2	29.9	93.9	93.6	93.2	94.1	39.2	20.4	19.8	11.2
6	5.9	6.0	6.6	6.4	4.8	4.8	6.6	6.4	174.9	95.5	38.6	12.7	96.4	96.5	96.7	96.7	69.8	63.6	21.6	3.0
7	10.2	10.3	11.1	9.4	10.4	11.1	11.7	11.4	944.8	582.3	303.2	52.5	93.2	91.7	90.9	90.7	1.8	0.4	0.4	0.4
8	17.2	18.0	19.4	19.4	16.4	17.0	17.88	19.1	874.8	354.3	176.7	64.0	88.6	84.8	79.6	73.1	18.8	6.0	1.6	0.0
9	9.7	8.5	6.4	7.6	9.0	8.7	7.7	7.7	142.1	69.0	24.9	5.0	96.4	96.3	96.4	96.4	23.6	8.4	2	0.6

10 References

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