A comparison of the hydrology, hydrochemistry and aquatic carbon flux from intact, afforested and restored raised and blanket bogs

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Declaration and author contributions

The candidate confirms that the work submitted is their own, except where work which has formed part of jointly authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

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Contributions: All authors agreed on the outline scope of the study. TH designed the sampling strategy, collected and analysed the data and wrote the manuscript. The co-authors critically assessed drafts and suggested edits and improvements. PC and JH assisted in developing the laboratory protocols. NS helped secure necessary permissions for the Forestry Commission study sites.

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Contributions: All authors agreed on the outline scope of the study. TH designed the sampling strategy and collected and analysed the field data. NS and RA helped secure necessary study site permissions and with local site knowledge. NS and PC set up help from the Scottish Environment Protection Agency (SEPA) to undertake laboratory analysis of the streamwater samples. All authors contributed to the methodology and interpretation of the analysis. PG helped with some of the sample collection for the Flow Country location. TH wrote the initial manuscript, and all co-authors critically assessed drafts, suggested edits and improvements and approved the final version for submission.

Thesis by alternative format rationale

This thesis follows the University of Leeds Faculty of Environment protocol for the format and presentation of an alternative doctoral thesis style, including published material. The project research questions were investigated using a range of approaches, which made the presentation of the data as four individual manuscripts appropriate. Two of the manuscripts have been published, and the final two manuscripts are in the advanced stages before submission to a journal. Therefore, the main body of the thesis consists of the manuscripts that are published, in review after minor editorial revisions or awaiting submission. An introduction, which provides background information, reviews relevant literature, and outlines the thesis aim and objectives, precedes the manuscripts. A synthesis chapter, bringing together the findings of the four manuscripts and discussing them in the context of the research questions, concludes the thesis.

Copyright declaration

Acknowledgements

Abstract

Peatlands store more carbon than any other terrestrial ecosystem and deliver important water regulatory ecosystem services. The loss of formerly accumulating peatlands to forestry and potential effects on the global climate have led to increased restoration initiatives. Forest-to-bog restoration, where coniferous forestry on bogs is clear-felled and other re-wetting measures implemented, is becoming more widespread. However, while the intention is to restore the pre-afforestation ecosystem function, little is known about the impacts on peat properties, hydrology and hydrochemistry. This thesis sought to improve the understanding by comparing intact, afforested and restored bogs at raised and blanket bog locations in Scotland. Monitoring over 18 months revealed that mean water-table depth in the afforested bogs (28.1 cm) was significantly deeper than intact bogs (9.7 cm) but shallower than the afforested bogs in the oldest restoration sites (12.4 cm). Peat bulk densities were significantly higher in the afforested bogs, and moisture and carbon content were slightly lower than intact bogs. Lower bulk density and greater moisture content in the restored peat than the afforested peat indicated peat swelling might occur as pores reopen after restoration. Higher total solutes in the porewater and streamwater of afforested bogs were evidence of aerosol scavenging from the trees. In contrast, elevated dissolved organic carbon (DOC) and phosphate (PO_4-P) in the restored bogs were from the felled waste (brash). Water yield was 18% lower in the afforested than the intact systems, reflecting the influence of evapotranspiration from growing tree stands. However, there were fewer differences in the peat properties, hydrological functioning and hydrochemistry between the intact bogs and the oldest restoration sites (10 - 17 years) than between the intact, afforested and most recent restoration sites (5 - 6 years), particularly where drain and furrow blocking had taken place.

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Abbreviations and symbols

AB	Afforested Bog
AET	Actual evapotranspiration
AirT	Air temperature
Al	Aluminium
ANOVA	Analysis of variance
BB	Blanket Bog
BD	Bulk Density
BFI	Baseflow index
C	Carbon
Ca	Calcium
Cl	Chloride
CLD	Compact Letter Display
CO_2	Carbon dioxide
CRM	Certified Reference Material
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
E4:E6	Ratio of spectral absorption 465 nm:665 nm
EC	Electrical Conductivity
Fe	Iron
FM	Flanders Moss, raised bog, Stirlingshire
FO	Forsinain, Flow Country
GIS	Geographical Information Systems
H^+	Hydrogen ion
ha	Hectare
IB	Intact Bog
IR	Ironhirst Moss, Dumfries
K	Potassium
K_s	Saturated hydraulic conductivity
Lat	Latitude
LiDAR	Light detection and ranging
Lon	Longitude
Mg	Magnesium
Mn	Manganese

N	Nitrogen / total number of samples
Na	Sodium
NH_4-N	Ammonium as nitrogen
NMR	Nuclear Magnetic Resonance
NNR	National Nature Reserve
NO_2-N	Nitrite as nitrogen
NO_3-N	Nitrate as nitrogen
NPK	Nitrogen, phosphorus and potassium
OS	Ordinance Survey
P	Phosphorus / precipitation
PC	Principal Component
PCA	Principal Component Analysis
PO_4-P	Phosphate as phosphorus
PTEs	Potentially Toxic Elements
PVC	Polyvinyl chloride
PW	Porewater
Q	Discharge
r	Non-parametric effect size
R	Restored, previously afforested, bog
R1	Oldest restoration site at the given bog location
R12	12-hour water table recession rate (cm h^{-1})
R2	Youngest restoration site at the given bog location
R6	6-hour water table recession rate (cm h^{-1})
RB	Raised Bog
r_s	Spearman rank correlation coefficient
RSPB	Royal Society for the Protection of Birds
S	Sulfur
SD	Standard Deviation
SE	Standard error of the mean
SEPA	Scottish Environment Protection Agency
$SUVA_{254}$	Specific UV absorption (spectral absorption at 254nm/DOC concentration)
SW	Streamwater
S_y	Specific yield
TA	Talaheel, Flow Country

Temp	Temperature
THM	Trihalomethane
TN	Total Nitrogen
TON	Total Oxidised Nitrogen
TP	Total Phosphorus
UK	United Kingdom
WTD	Water-table depth
Yr	Year
η^2	Eta squared effect size

Chapter 1: Introduction

1.1 Significance of peatlands

Peatlands are wetland ecosystems where a layer of peat exceeding 30 – 40 cm thickness accumulates on the surface, largely consisting of partially decomposed plant remains, with slow decomposition rates due to waterlogged conditions (Charman, 2002). The semi-decomposed plant material mostly consists of sedges, grasses, and mosses, although woody shrubs may also be present, along with trees, particularly in tropical peatlands (Bonn *et al.*, 2016). The accumulation of dead plant material results in an imbalance in the nutrient and carbon cycles where primary production of carbon and nutrients exceeds that of microbial decomposition, leading to net carbon sequestration over millennia. While peatlands are only thought to cover 2.84% of the Earth's landmass (Xu *et al.*, 2018b), they store more carbon than any other terrestrial ecosystem (Joosten *et al.*, 2016) and constitute a third of the global soil carbon pool (Scharlemann *et al.*, 2014; Yu *et al.*, 2010). Peatlands also provide other valuable ecosystem services (Bonn *et al.*, 2016), supporting a unique habitat for wildlife (Minayeva *et al.*, 2017), freshwater supplies (Xu *et al.*, 2018a), flood reduction in some settings (Acreman & Holden, 2013), and recreational opportunities (Anderson *et al.*, 2016). However, peatlands are sensitive systems, which require specific climatic conditions and poor drainage to sustain carbon sequestration. Changes in land use and climate can disrupt this balance, altering the hydrology and hydrochemistry and the ecosystem services delivered. Plantation forestry has led to significant loss of formerly accumulating peatland landscapes, and as such new initiatives to clear-fell and re-wet afforested peatlands are becoming more widespread. Forest-to-bog restoration is an example that intends to restore the pre-afforestation ecosystem function of rain-fed peatlands (bogs), which is important for carbon sequestration, water regulation, and the wildlife they support.

This chapter introduces peatland types and two rain-fed (ombrotrophic) peatland classifications that are the focus of this research: raised bogs and blanket bogs. Their distribution, both globally and in the UK, and defining characteristics are described. Land-use change impacts on natural bog function are highlighted, particularly from

plantation forestry, and the extent of drainage for forestry is given globally and in a UK context. The literature on how afforestation of bogs has affected peat physical and chemical properties, hydrological functioning and hydrochemistry is reviewed and summarised. Then the techniques used to clear-fell and restore afforested bogs, known as forest-to-bog restoration, are outlined. As this is a relatively new type of peatland restoration, studies from the forestry literature are also reviewed to provide evidence for likely impacts of forest-to-bog restoration on peat properties, hydrology, and the hydrochemistry of porewater and streamwater. Research gaps are identified, and the overall aim and objectives of the thesis will be presented before the research approach, study location and methodology are summarised. Finally, this chapter ends with an outline of the remaining structure of the thesis and subsequent chapter contents.

1.2 Peatland types

Ombrotrophic peatlands, commonly referred to as bogs, receive most of their water and solutes from precipitation. Bogs are typically low in solutes and nutrient-deprived or oligotrophic since the underlying geology does not dominate their chemistry; fens are more nutrient-rich and typically support a greater diversity of plant communities. The oligotrophic nature of bogs means they are acidic with a pH between 3.5 and 4.5 (Lindsay, 1995), and as a result, they can only support plant communities that can tolerate the acidity. Minerotrophic peatlands, or fens, receive water through both precipitation and more mineral-rich groundwater influx (Lindsay, 1995), with a predominance of the latter. In contrast to bogs, the pH of fens can vary between 4.0 and 9.0 (Lindsay, 1995), becoming more alkaline if exposed to calcareous substrates (Tahvanainen, 2004). Streams draining bogs and fens may also be coloured due to the presence of dissolved organic matter (DOM), although higher concentrations of dissolved organic carbon (DOC) are often associated with fens (Haapalehto *et al.*, 2014; Koskinen *et al.*, 2011; Koskinen *et al.*, 2017; Olefeldt & Roulet, 2012) as the solubility of DOC increases with pH (Clark *et al.*, 2009; Clark *et al.*, 2005). However, while DOC concentrations may be lower in bogs, higher concentrations can occur in degraded systems (Evans *et al.*, 2016; Parry *et al.*, 2015).

1.3 Raised and blanket bogs

Two bog classifications include raised bogs, typically found in a lowland setting, and blanket bogs often associated with UK uplands but may also be found at lower elevations (Figure 1-1). Blanket bogs are the dominant bog classification in the UK, but there is a wider distribution of raised bogs in other parts of the world (Tahvanainen *et al.*, 2016). In the UK, the coverage of raised bogs has been estimated to be 69,664 ha, although only 3,836 ha remain intact (Lindsay & Immirzi, 1996). In contrast, blanket bogs occupy 2,196,700 ha (Bita-Nicolae *et al.*, 2016), representing ~10% of the worldwide blanket bog distribution (Tallis *et al.*, 1997). Raised bogs have a characteristic dome shape (Figure 1-2) with a gentle gradient, often due to the terrestrialisation process, where shallow lakes or hollows become dominated with fen vegetation, eventually leading to a rising mound of rain-fed bog peat (Lindsay, 1995). Peat depths in the dome's centre can often exceed those found in blanket peatlands, and runoff from streams, springs and floods may not reach the surface in undamaged ombrotrophic areas of raised bogs except in surrounding 'lagg fens' (Figure 1-2), where there is a transition from bog to fen (Charman, 2002). Where peat has formed over other substrates, local flow systems may develop under water-table mounds and when sufficiently large for water to enter the mineral horizons, minerotrophic groundwater is forced under artesian pressure to surrounding fens (Siegel, 1983). The resulting water's chemical composition may inhibit the bog from spreading further over the fen since the peat-forming mosses are intolerant of the higher pH and minerals such as calcium (Siegel, 1983).

Figure 1-1 – Fringes of an intact lowland raised bog where it meets agricultural land, Flanders Moss, southern Scotland (left). Intact blanket bog covering most of the landscape with natural pools, Flow Country, northern Scotland (right).
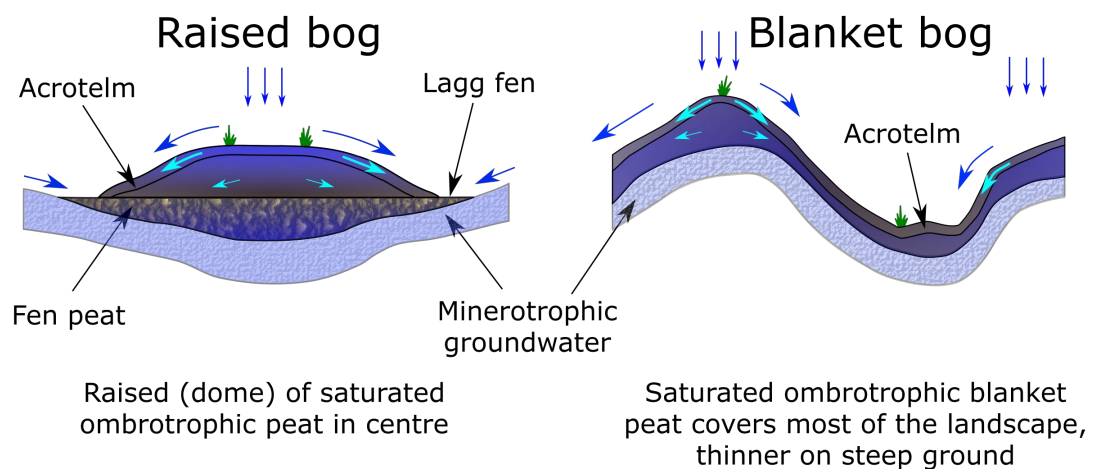
Figure 1-2 – Raised and blanket bog characteristics - showing the ombrotrophic peat's isolation from the minerotrophic groundwater. Note the characteristic dome shape of the raised bog has been exaggerated, and the gradient is often very gentle (e.g., Flanders Moss has multiple domes with changes in elevation 2 – 6 m over 0.5 – 1 km). Water flow may be across the surface as overland flow, through the near-surface more permeable peat (acrotelm), or a small amount of lateral seepage can occur in the denser layers (catotelm). Modified from Charman (2002).

Blanket bogs can cover large areas of both sloping and flat terrain in regions with annual mean precipitation greater than 1000 mm (Lindsay *et al.*, 1988) and suitably poor sub-surface drainage (Holden *et al.*, 2017). The maritime climates of regions like

the British Isles and Newfoundland can provide ideal conditions for a blanket bog to develop (Gallego-Sala & Colin Prentice, 2013), particularly in the uplands (Price *et al.*, 2016), where there can be a large excess of precipitation over evapotranspiration (Godwin, 1981). Traditionally, water flow in bogs has been perceived to flow across the surface as overland flow or through the shallow, more permeable subsurface layers. Little flow was thought to occur in deeper, denser peat. Since water tables are often within a few cm of the peat surface (Evans *et al.*, 1999), a high percentage (~80%) of the flow in blanket peatlands has been shown to run across the surface as saturation-excess overland flow, with only 10% through the near-surface layers (Holden & Burt, 2003b). However, the rich vegetation and natural microforms of hollows and hummocks associated with intact bogs attenuate flow across the surface (Grayson *et al.*, 2010; Holden *et al.*, 2008). Both blanket bogs and raised bogs have a flashy response to rainfall due to the shallow water tables, but since slopes are usually less severe in raised bogs, streamflow response is more subdued (Bay, 1969; Evans *et al.*, 1999; Holden & Burt, 2003b; Holden & Burt, 2003c; Spieksma, 1999). In dry periods discharge declines rapidly in raised bogs, and water yield may be significantly less than that in blanket bogs (Holden & Burt, 2003c; Spieksma, 1999).

Hemond (1980) found that bog ecosystems accumulate metals from precipitation by ion exchange, which increases the bog's mineral acidity but only modestly compared to other processes. The main ions associated with ion exchange in the peat are the base cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) which are readily attracted to negatively charged humus particles displacing H^+ ions (Clymo, 1963). Acid rain inputs are a significant contributor to bog acidity but may be suppressed by biological processes within the bog, particularly the reduction of sulfate and nitrate uptake (Hemond, 1980). Evapotranspiration also plays a role in maintaining concentrations of ions in the peat. Hemond (1980) suggested that the largest contribution to bog acidity was from humic acids derived by the decomposition of *Sphagnum* mosses. Nutrient concentrations are generally low in intact bogs and limited to inputs from precipitation. Intact bogs typically retain nutrients since the microbial processes responsible for mineralisation are inhibited by the shallow water tables and the bog's capacity to accumulate organic matter (Price *et al.*, 2016).

Due to the slow decomposition rates through shallow water tables, peat in intact bogs usually has low dry bulk density, high porosity and moisture content, and surface layers often consist of a thick layer of living and partially decomposed plant matter (Mustamo *et al.*, 2016). Bulk density and the degree of humification typically increase with depth as larger plant fragments break down into amorphous peat (Rezanezhad *et al.*, 2016). Hydraulic conductivity (or permeability) is generally low but may increase in the less decomposed surface layers or with the presence of macropores (Wallage & Holden, 2011). Studies have found strong negative correlations between hydraulic conductivity and bulk density and the amount of organic material in the peat (Kolka *et al.*, 2011; Morris *et al.*, 2019). The traditional diplotelmic model used to describe peatlands assumed little lateral variability in peat properties and a clear distinction between the near-surface (acrotelmic) peat and the deeper (catotelmic peat). However, more recent studies suggest that significant variability can occur laterally and throughout the soil profile, suggesting that the model is too general and should be treated with caution (Baird *et al.*, 2016).

1.4 Forested peatlands

Historically, peatlands have been subject to different land management changes (Curtis *et al.*, 2014; Reed *et al.*, 2009) as they have not always been viewed as profitable in their natural condition (Martin-Ortega *et al.*, 2017). Drainage for pasture, agriculture or planting non-native trees on open peatlands for timber (Päivänen & Hånell, 2012) or palm oil production (Kho & Jepsen, 2015; Sangok *et al.*, 2017; Tonks *et al.*, 2017) have resulted in significant losses of formerly accumulating peatlands (Andersen *et al.*, 2017; Holden *et al.*, 2004; Menberu *et al.*, 2016; Parry *et al.*, 2014). Approximately 12% of global peatlands and 44% of European peatlands are no longer accumulating new peat (Joosten, 2016).

In the boreal countries of Finland, Russia, Norway, and Sweden, 100,000 km^2 (Simola *et al.*, 2012; Strack, 2008) of fen and bog peatlands have been drained for forestry to supply timber, wood fuel and pulp. More than half of Finland's formerly accumulating peatlands have been drained, and large areas afforested between 1960 and 1990

(Strack, 2008). In the UK, non-native coniferous trees have been planted on previously open peatlands since the 1940s (Curtis *et al.*, 2014; Reed *et al.*, 2009), but, as in the boreal zone, most of it occurred in the 1970s and 1980s when developments in cultivation and ploughing techniques elevated it to an industrial-scale process. Up to ~190,000 ha of deep peat and ~315,000 ha of shallow peat was afforested in the UK between 1950 and the 1980s (Cannell *et al.*, 1993; Hargreaves *et al.*, 2003). The rate of afforestation in the UK during the 20th century accelerated after the First World War with a strategic drive to increase timber production by establishing the Forestry Commission in 1919 and a rise in forestry investment firms, who took advantage of government tax incentives (Bateman, 1992). Private forest investment was consistently used as a tax refuge from income earned from other sources and peaked in the 1980s; economic problems had previously stunted private sector growth. While public sector forestry had started to decline in the 1980s, it was compensated for by a threefold increase in private woodland. Concern over the damage this was inflicting on the environment led to the tax reliefs being abolished in 1988 (Anderson & Peace, 2017; Bateman, 1992), which ultimately led to a reduction in the rate of afforestation on UK peatlands.

Afforestation has led to the fragmentation and loss of connectivity between important wildlife habitats (Anderson *et al.*, 2016) as trees have encroached on the once open landscape. In the Flow Country in northern Scotland (the largest blanket bog area in Europe), this was sufficient reason for the 1988 change in policy as it threatened protected bird species. The Royal Society for the Protection of Birds (RSPB) is now actively trying to reverse the effects of afforestation through restoration measures and has a new field centre to assist ongoing research into the restoration of these peatlands at Forsinard in the Flow Country. Regarding policy changes, the UK Forestry Standard (Forestry Commission, 2017) now discourages planting new forestry on land with a peat depth greater than 50 cm and restoration work at designated sites is actively promoted (Patterson & Anderson, 2000). Similarly, no further drainage for forestry occurs in Finland, Sweden and Russia (Joosten, 2016) and earlier measures were taken in parts of Belgium. In the forests of Wallonia, it is forbidden to plant new forestry in

peat soils at a depth greater than 40 cm and in the vicinity of springs (Andersen *et al.*, 2017).

1.4.1 Potential peat carbon losses through forestry

Globally, peatlands cover around 4.23 million km^2 (Xu *et al.*, 2018b) and are estimated to store 450 Gt of carbon (Joosten, 2009). Boreal and subarctic peatlands store more carbon (419 Gt) than areas of equivalent forestry (including dead wood and soil organic matter), over a 2.6 million km^2 area (Apps et al., 1993). Intact, UK peatlands have been estimated to contain 20 times more carbon, per hectare, than the average commercial forest plantation (Fenton, 2010). Forestry on peat is thought to cause the peat to dry and carbon to be lost to the atmosphere through aerobic decomposition. However, forestry captures atmospheric carbon that becomes stored in the wood, tree litter and forest soils. Cannell *et al.* (1993) suggested yield class 12 Sitka spruce (*Picea sitchensis*) stores 16.7 kg C m^{-2}, equivalent to 35.5 cm of deep peat or 20.6 cm shallow peat, but if planted on substantially deeper peats, could result in a net loss of carbon. A later study by Hargreaves *et al.* (2003) found peat losses through decomposition may be lower than first thought (1 t C ha^{-1} yr^{-1}), but afforested peatlands in Scotland would only continue to sequester more carbon than is lost from the peat for a limited time (90 – 190 years). Therefore, much of the afforested deep peat (> 50 cm deep) illustrated in Figure 1-3 may potentially be losing carbon in the next 50 years if no further action is taken.
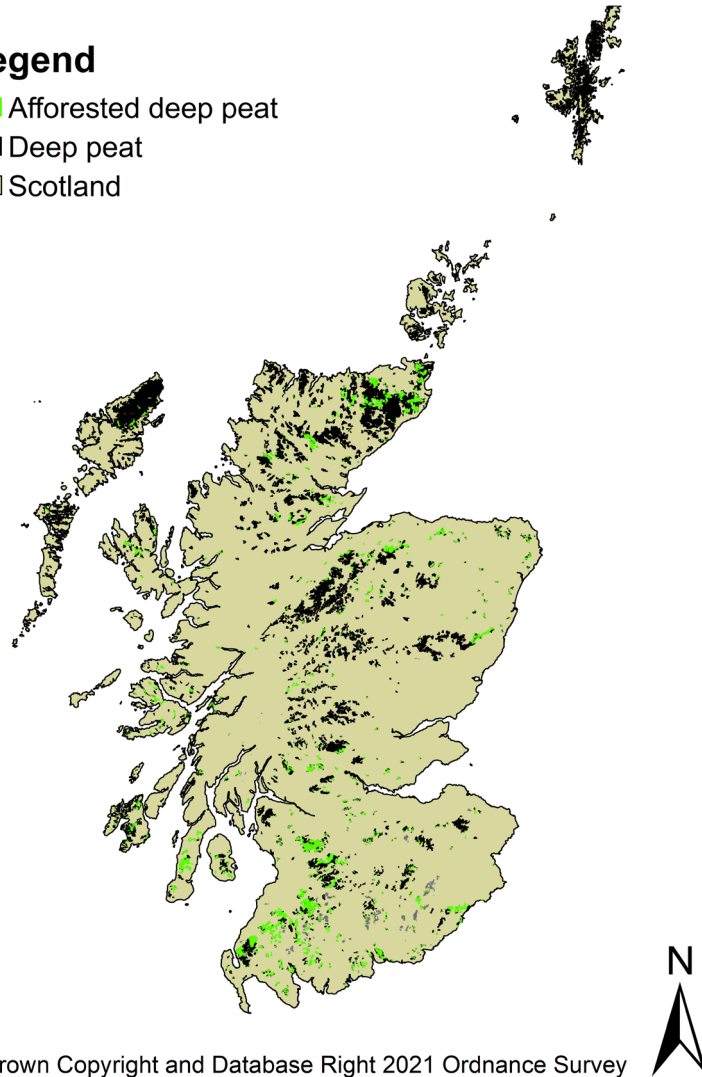
Figure 1-3 – Extent of afforestation on deep peat in Scotland – Soil data were taken from the James Hutton Institute and the National Forest Inventory Scotland 2015 used for forest coverage.

1.4.2 Impacts of peatland forestry on hydrology and peat properties

Preparation of the peat for afforestation involved ploughing and excavating drainage channels. Drainage lowers the water table (Anderson & Pyatt, 1986; Anderson *et al.*, 2000; Anderson & Peace, 2017), further reduced by increased evapotranspiration from the planted trees as they mature (Anderson & Pyatt, 1986; Nisbet, 2005). As such, reductions in annual runoff have been reported from afforested peatlands (Birkinshaw *et al.*, 2014; Robinson, 1998). Lower water tables also impact the peat's physical structure, as more of it becomes exposed to the air (see the difference between fresh and oxidised peat, Figure 1-4). Maintaining a near-surface water table is one of the most important characteristics for the ecology and biogeochemistry of bogs (Joosten *et*

al., 2016). When the peat is well aerated, the accumulation of new peat virtually ceases, and the increased oxidation releases more carbon dioxide into the atmosphere (Hargreaves *et al.*, 2003).

The drying of the surface peat and subsequent compaction of the lower layers can lead to subsidence and an increase in bulk density (Anderson & Peace, 2017; Camporese *et al.*, 2006; Gebhardt *et al.*, 2010; Leifeld *et al.*, 2011; Minkkinen & Laine, 1998; Price & Schlotzhauer, 1999; Shotbolt *et al.*, 1998; Silins & Rothwell, 1998; Sloan *et al.*, 2019). Increases in bulk density are often associated with reductions in hydraulic conductivity as pores collapse (Holden *et al.*, 2014; Kolka *et al.*, 2011; Rycroft *et al.*, 1975). Conversely, desiccation cracks and enlargement of macropores (Holden *et al.*, 2001) through increased aeration and enhanced evapotranspiration from the trees may increase hydraulic conductivity and infiltration rates. The degree of peat humification (decomposition), often measured in the field by the von Post (1922) 10-point scale or colorimetric methods (Chambers *et al.*, 2011), will increase due to increased aeration with deeper water tables (Cannell *et al.*, 1993). More humified peat may lead to a decline in pore sizes and reduced hydraulic conductivity as spaces between larger fragments of plant material decrease when broken down into amorphous peat (Rezanezhad *et al.*, 2016).

Figure 1-4 – Fresh peat taken from Flanders Moss West (left) and exposed dried, cracked peat at Talaheel, Flow Country (right).

Flood risk resulting from the disturbance associated with afforesting peatlands with coniferous species was debated in the UK as many plantations matured. One of the longest-running afforested peatland studies was the Coalburn catchment in Northumberland, which observed baseflows to double, increased annual streamflow and reduced peak lag times with initial drainage (Robinson, 1986, 1998). However, a more subdued regime ensued as the trees matured and evapotranspiration losses increased (Birkinshaw *et al.*, 2014). Other field studies on the hydrological effects of afforestation on peatlands have been undertaken (Archer, 2003; Bathurst *et al.*, 2018; Robinson *et al.*, 2003; Robinson *et al.*, 2013), yet only two paired catchment studies have compared a near 100% afforested and near-by 100% open peatland (Bathurst *et al.*, 2018; Marc & Robinson, 2007). To my knowledge, the effects of forest-to-bog on the hydrological function of raised and blanket bogs have not been studied; thus, more research is needed in this area.

Changes in hydraulic conductivity will have implications for the rainfall response of catchments since subsurface flow in bog systems typically occurs through near-surface, more permeable layers (Evans *et al.*, 1999; Holden & Burt, 2003a; Holden & Burt, 2003c) except where there are soil pipes (Holden, 2009; Holden *et al.*, 2001). The practice of drainage alone has been shown to affect the peat's physical properties, the catchment's response to rainfall (Archer, 2003; Ballard *et al.*, 2012; Holden *et al.*, 2004; Holden *et al.*, 2011), and the hydrochemistry (Holden *et al.*, 2004; Ramchunder *et al.*, 2009). A conceptual diagram of some of the different processes affecting the peat properties, hydrology and water quality when intact bogs are afforested and subsequently restored is given in Figure 1-5, highlighting known research gaps.
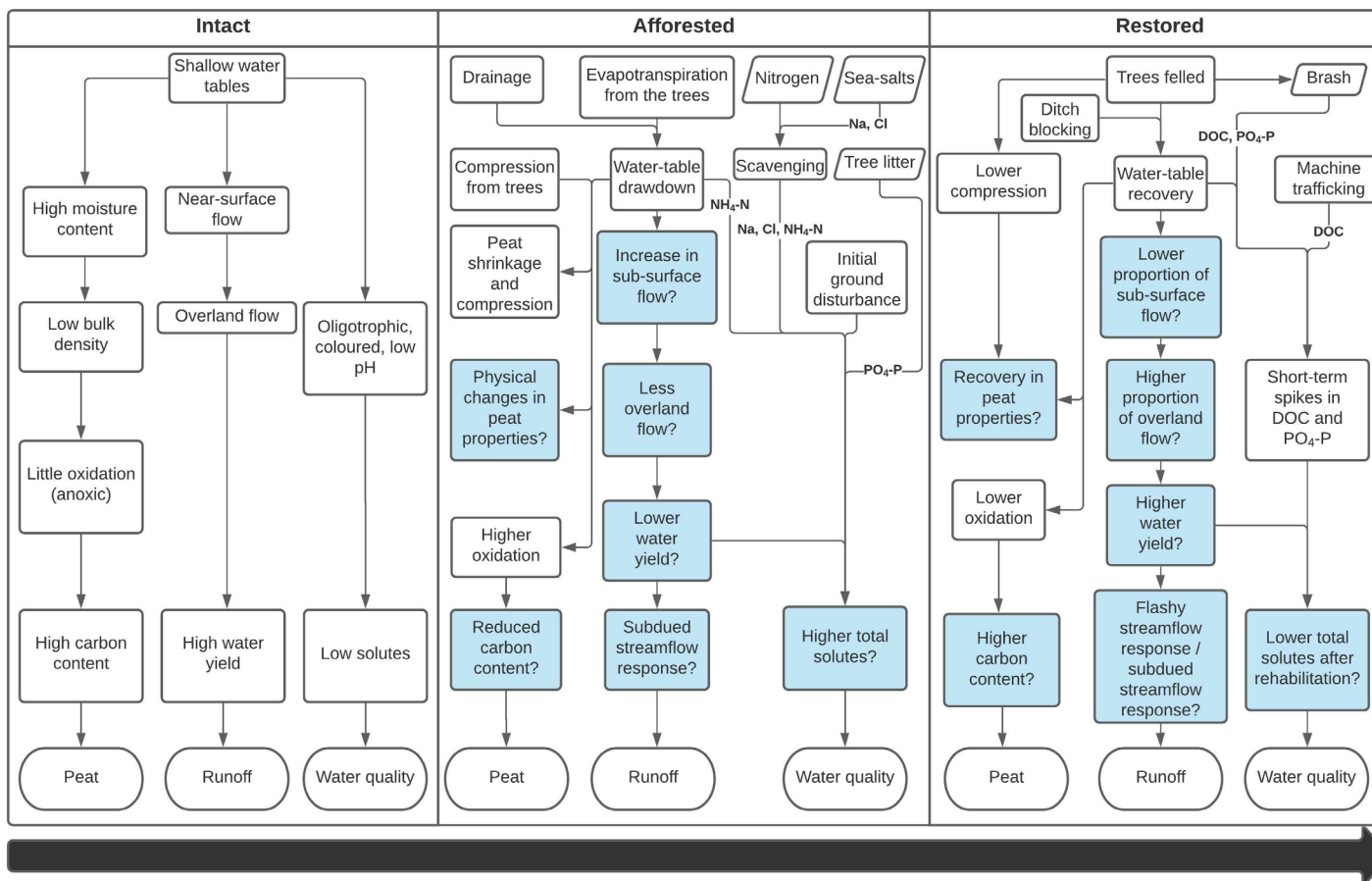
Figure 1-5 – Conceptual diagram of some of the different processes in intact, afforested and restored bogs affecting peat properties, hydrology and hydrochemistry. Knowledge gaps are highlighted in blue.

The changes brought about by afforestation and the subsequent restoration of peatlands on the water balance may be quite severe, and it is still unclear how they affect peatland hydrological functioning. Significant knowledge gaps need to be filled to influence future policies on which restoration techniques result in the best outcome for the delivery of wider ecosystem services (Anderson *et al.*, 2016). For example, we do not know how the restoration of previously afforested peatlands influences river flow regime, river water quality or aquatic carbon flux. The latter can have carbon implications for carbon losses and gains in peatlands. Therefore, further soil carbon assessments are needed to determine if restoration is likely to fulfil future carbon sequestration objectives.

1.4.3 Impact of peatland forestry on water quality

Forestry practices can disturb the peat physically and biogeochemically through ploughing and drainage, tree thinning and harvesting operations, replanting and road construction. Streams draining afforested catchments may have elevated concentrations of nutrients, organic carbon, potentially toxic elements (PTEs), major ions, and increased acidity (Cummins & Farrell, 2003a, 2003b; Drinan *et al.*, 2013b; Harriman, 1978; Harriman & Morrison, 1982; Harriman *et al.*, 1987; Harriman *et al.*, 2003; Neal *et al.*, 2004; Nisbet & Evans, 2014; Nisbet *et al.*, 1995). Williamson *et al.* (2021) found peat cover and upland plantation forestry to be major positive controls on riverine exports of DOC, with afforestation thought to have raised British exports of DOC by 0.168 Tg C yr^{-1}. Initial drainage and the use of heavy machinery can change the structural composition and redox conditions within the peat, resulting in the increased mineralisation of carbon, nutrients and the mobilisation of PTEs (Drinan *et al.*, 2013b; Harriman & Morrison, 1982; Harriman *et al.*, 2003), but the effects after re-wetting are still unclear. Forestry operations such as clear-felling have been linked to pulses in organic carbon and nutrients (Cummins & Farrell, 2003a, 2003b; Nieminen *et al.*, 2017), so there are likely short-term effects of forest-to-bog restoration on water quality, but longer-term effects are not known.

Internal nutrient cycling in bogs is essential because nutrients are mainly received from precipitation, and nutrient cycling changes are tightly coupled to the carbon cycle (Aerts *et al.*, 1999; Gaffney *et al.*, 2018; Keller *et al.*, 2006; Oviedo-Vargas *et al.*, 2013). Water-table drawdown in afforested bogs disrupts the natural balance through changes in redox conditions, stimulating microbes responsible for the ammonification and nitrification processes (Adamson *et al.*, 1998; Daniels *et al.*, 2012; Drinan *et al.*, 2013b; Macrae *et al.*, 2013). Typically, ombrotrophic bog peat is nutrient-poor, but when aerated through drainage, can release inorganic forms of N from organically bound nitrogen in the peat, usually in the form of NH_4-N (Gaffney, 2017; Holden *et al.*, 2004; Miller *et al.*, 1996; Urbanová *et al.*, 2011) as pH restricts nitrification and the production of NO_3-N. However, when NH_4-N leaches from the porewater into streams, it readily oxidises to NO_3-N and is quickly taken up by flora and fauna (Hemond, 1983; Howarth, 2014) that are N limited. Therefore, reports of excess NO_3-N in runoff are generally limited to minerotrophic fens (Koskinen *et al.*, 2017), where the peat is more nutrient-rich due to groundwater inputs (Lindsay, 1995) and nitrification is not constrained by low pH (Dancer *et al.*, 1973).

Scavenging of aerosols from the atmosphere by tree canopies (Dunford *et al.*, 2012; Neal *et al.*, 1992; Neal *et al.*, 2004; Nisbet *et al.*, 1995), particularly S and N compounds, resulted in increased acidity and aluminium concentrations in porewater and streamwaters of afforested peatlands with subsequent impact on stream invertebrates, fish and birds (Baker & Schofield, 1982; Curtis *et al.*, 2014; Harriman & Morrison, 1982; Harriman *et al.*, 1987; Neal *et al.*, 1992; Ormerod *et al.*, 1989; Sparling & Lowe, 1996). Scavenging of sea salts has also been shown to increase streamwater acidity by displacing H^+ and Al^{3+} ions from forest soils (Drinan *et al.*, 2013b; Harriman *et al.*, 2003). NPK fertilisers typically used to promote early tree growth (Drinan *et al.*, 2013a; Harriman, 1978; Lu & Tian, 2017; Miller *et al.*, 1996; Shah & Nisbet, 2015) may persist in streamwater for greater than 10 years after their application (Kenttämies, 1981). While the trees would sequester most of the fertiliser applied, any excess may have implications for potential eutrophication from phosphorus loads since the peat's low phosphorus adsorption capacity will mean it is not retained (Asam *et al.*, 2014b; Kaila *et al.*, 2014; Rodgers *et al.*, 2010). However,

the small number of forest-to-bog restoration studies and the limited opportunity to measure long-term effects make it difficult to determine whether there will be legacies of plantation forestry after restoration.

1.5 Afforested deep peat in the UK

The early UK attempts to afforest bogs date back to 1730 (Paavilainen & Päivänen, 1995). Cannell *et al.* (1993) estimated that 9% of deep peat in the UK had been drained and planted with mostly Sitka spruce, *Picea sitchensis* (Figure 1-6), and lodgepole pine, *Pinus contorta*, between the 1940s and the 1990s. Ploughing of the peat surface results in variations in surface microtopography with ridges and furrows. Trees are typically planted in the ridges, while furrows can provide additional drainage, although larger drains are excavated to channel the water away from whole forest blocks. Since peat soils are low in nutrients, it was customary to apply phosphate fertilisers to promote early tree growth (Shah & Nisbet, 2015) and help establishment.

The extent of afforestation on deep peat in Scotland was shown in Figure 1-3. Out of an estimated 764,000 ha of deep peat, ~111,000 ha is planted with woodland: ~54,000 ha on the Public Forest Estate (i.e. government-owned). Thus, almost 15% of deep peat is afforested in Scotland, according to these estimates. There is an estimated 680,000 ha of deep peat in England, ~51,000 ha of which is afforested, and ~21,000 ha is on the Public Forest Estate (Anderson *et al.*, 2014). In Wales, deep peat soils cover approximately 116,000 ha, ~18,000 ha of which is afforested and ~11,000 ha owned by the Welsh government (Vanguelova *et al.*, 2012).

Figure 1-6 – Coniferous plantation forestry on a blanket bog in the Flow Country, planted in the 1980s. The trees are largely Sitka spruce (Picea sitchensis).

By the year 2000, the conservation and wider environmental benefits of peatlands were becoming more widely recognised. In the same year, the UK Forestry Commission published new policy guidelines for peatland habitats, specifically for raised and blanket bogs (Patterson & Anderson, 2000). The guidelines stated that future grants for new planting or natural regeneration proposals on active raised bogs and extensive areas (> 25 ha) of active blanket bog, where peat depths exceeded 1 m, would no longer be approved. Furthermore, authorisation was given to prevent new planting where peatland habitats risked being damaged and to request unauthorised deep peat plantations were restored. At that time, not enough evidence was available to support widespread restoration efforts. However, what is now known as forest-to-bog restoration was subsequently considered a management option for afforested bogs, where there was a chance that natural peatland ecosystem functions could be restored (Scottish Forestry, 2015).

1.6 Forest-to-bog restoration

1.6.1 Forest-to-bog restoration processes

Future Scottish Forestry guidelines on whether felled plantations on peatlands should be restocked or restored are dependent on the site's ecological status (Figure 1-7). Restoration processes vary (Table 1-1) but continue to evolve with Forest Research and the RSPB developing new trials to advance current methods such as ground smoothing and re-wetting of cracked peat (Anderson, 2017). Much of the research has been carried out on blanket peatlands in the UK, but in Fennoscandia, restoration has occurred on base-rich fens, and nutrient-poor raised bogs with different topography to many UK sites (Komulainen *et al.*, 1999; Laine *et al.*, 2011; Menberu *et al.*, 2016).
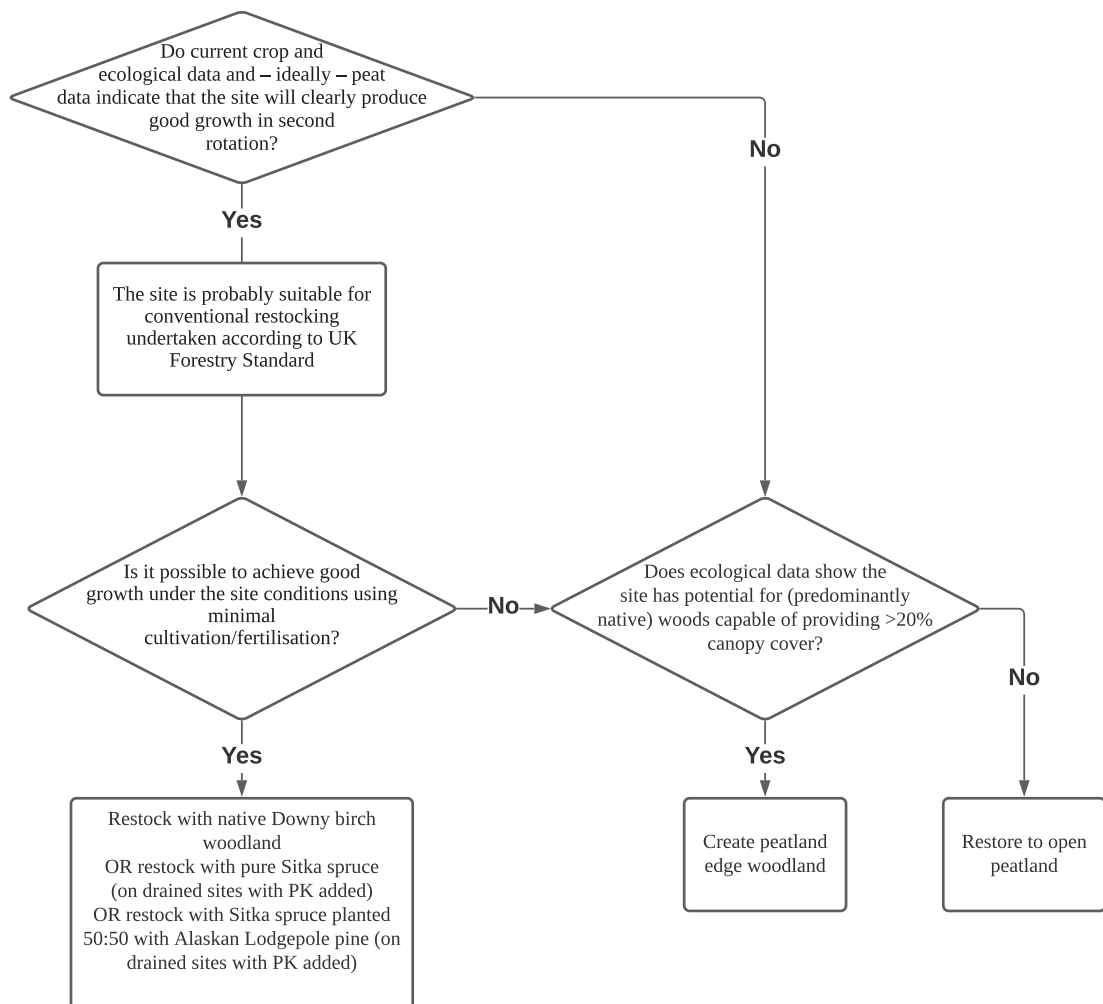
Figure 1-7 – Flowchart for future options on deep peat sites that are not already classed with a presumption to restore biodiversity or for other reasons from Scottish Forestry (2015).

Table 1-1 – Common forest-to-bog restoration processes

Restoration processes	Description	Equipment	Advantages	Disadvantages
Felling-to-waste	Trees felled, and whole trees left on the surface or compressed into drains and furrows	Hand felling with chainsaws/mechanised harvester	Lowest cost - £250 ha^{-1} (Anderson, 2001)	Nutrient release from decomposing brash
Phased felling	Small areas of forest are felled at a time	Hand felling with chainsaws/mechanised harvester	Less impact on water quality	Not as efficient for forest clearance
Conventional harvesting	Trees felled and timber harvested	Mechanised harvester and forwarder	Timber is reused	Machine trafficking
Low-impact harvesting	A combination of phased felling and harvesting by winching out trees to reduce damage by machine trafficking	Hand felling with chainsaws/overhead skyline	Less soil and water damage	Not as efficient for forest clearance/cost
Whole-tree mulching	Trees are mulched from standing, and mulch spread across peat surface	Boom mounted masticator on large excavator	No further action required for timber and brash	Possibility of enhanced nutrient enrichment from the quantity and accelerated decomposition of mulched tree waste
Whole-tree harvesting	Entire trees are harvested, leaving little forest debris	Forwarders/winches/helicopters	Brash and timber removed	Cost – whole tree removal by helicopter £4300 - £9000 ha^{-1} (Anderson, 2001)
Use of brash mats	Felled debris used to construct mats for machine access routes	Chainsaws/mechanised harvester	Reduced damage to peat from machine trafficking	Require removal / however fewer alternatives in peatlands to prevent loss of machinery in bogs
Drain blocking	Collector drains blocked with plastic piling of peat dams	Plastic piling/excavator	Speed up water table recovery	Further machine trafficking and peat disturbance
Furrow blocking	Furrows blocked typically with peat dams	Excavator	Speed up water table recovery	Further machine trafficking and peat disturbance
Stump flipping	Tree stumps are removed from ridges and left to decompose	Excavator	Help smooth out the ground surface	Further peat disturbance
Ground smoothing	Ridges and furrows are smoothed out to create a level surface	Excavator	Help smooth out the ground surface	Further peat disturbance

Tree removal is a necessary first step in the forest-to-bog restoration process. There are different tree removal methods on bogs which are a trade-off between environmental concerns and economics. The costs associated with removing logging debris from peatland sites can be very high: removing whole trees (whole-tree harvesting) by forwarders, overhead cables (skylines) or helicopter range from £1250 to £9000 ha^{-1} (Anderson, 2001). The latter would most likely only be used where site access was difficult. In contrast, when trees are felled to waste (trees and debris just left to decompose), net costs can be as little as £250 ha^{-1} (Anderson, 2001).

The tree removal methods are dependent on the site characteristics, including tree growth and machinery access or whether outflows are into ecologically sensitive waters such as oligotrophic lakes. Where possible, the trees are harvested to generate revenue from the timber, but any valueless felled waste such as treetops and branches (brash) are usually left on site (conventional harvesting). Brash may be compressed into furrows or drains to slow water flow (Figure 1-8a) or naturally accumulate (Figure 1-8b). Brash may also be mulched with a mechanical masticator (Figure 1-8c) and spread across the peat's surface (Figure 1-8d) depending on the site's management strategy (Moffat *et al.*, 2006). However, other harvesting methods have been adopted where trees are felled in phases (Phased felling), and most of the brash is removed and chipped for biomass reducing environmental impacts. Typically harvesting utilises mechanised harvesters and forwarders for tree felling and removing timber for transport off-site. However, low impact harvesting (Shah & Nisbet, 2019) may be adopted where the trees may be winched out using skylines in ecologically sensitive areas. Where tree growth has been poor, making standard harvesting uneconomical, whole trees may be mulched from standing (whole-tree mulching) using a masticator mounted on the arm of an excavator (Muller *et al.*, 2015) and the mulch spread across the site.

Most forestry operations require heavy machinery; therefore, brash mats are used to protect the peat surface and reduce compaction. Brash mats also prevent machinery

from becoming stuck in the wettest areas of peat. Research has shown that the appropriate use of brash mats can effectively prevent additional peat damage, but they may be sources of nutrients if they remain on-site (Gaffney *et al.*, 2021; Moffat *et al.*, 2006; Rodgers *et al.*, 2010). Tree removal alone may not be sufficient to raise the water table to the same levels found in intact bogs. Therefore, drainage ditches and plough furrows are often infilled with peat or blocked with peat or plastic piling dams, typically used by peatland practitioners to raise the water-table level (Gaffney *et al.*, 2020b; Holden *et al.*, 2017). Peat dams (Figure 1-8e) have the advantage of only using natural materials found on-site. After blocking ditches and furrows, water pooling may occur behind the dams, which eventually block up with peat and may allow for the regeneration of *Sphagnum* mosses (Figure 1-8f). The main disadvantage of peat dam installation is the additional disturbance it causes, and the dams may degrade with time (Holden *et al.*, 2017). Sometimes plastic piling may be more appropriate (Figure 1-9), especially on steeper slopes. Attempts have been made in the UK to kill the trees by re-wetting alone, but trials were largely unsuccessful (Anderson & Peace, 2017). However, felling has not always taken place in Fennoscandia because many peatlands were naturally forested. Therefore, restoration here has often been limited to the infilling and blocking of drainage ditches (Koskinen *et al.*, 2011; Koskinen *et al.*, 2017; Menberu *et al.*, 2016; Sallantaus & Koskinen, 2012), with clear-felling only occurring where significant tree growth occurred since initial drainage. Anderson and Peace (2017) found clear-felling and the damming of drains and ploughed furrows to raise the water table to within 5 – 10 cm of the intact blanket bog after 10 years, but similar studies after forest-to-bog restoration are scarce.

(a) Remains of a tree in a forest drain, Flanders Moss (RBR1)

(b) Accumulation of mulch in a furrow (BBR2)

(c) Boom mounted mechanical masticator (RBR2)

(d) Five years after mulching at Forsinain, Flow Country (BBR2)

(e) Fresh peat dams on a main collector drain (BBR2)

(f) Sphagnum accumulation behind peat furrow blocks (BBR1), 17 years post-felling.

Figure 1-8 – Common restoration processes: brash handling (a – d); peat dams (e – f). Corresponding site code from chapters 3-5 are given in parentheses where RB = raised bog; BB = blanket bog; R1 = Oldest restoration site; R2 most recent restoration site.

Figure 1-9 – Use of plastic piling dams to attenuate runoff and raise the water table (Flanders Moss NNR, left; Forsinain (BBR2), right).

Another legacy from afforestation results from the ploughing of the original surface. Even after restoration, the plough ridges and furrows are still visible and might be more efficient at channelling water off the peat's surface. Therefore, there is a need to determine how the different microtopography responds to forest-to-bog restoration. Forest Research and the RSPB have trialled stump flipping and ground smoothing techniques (Anderson, 2017) that create a level surface, but there is a lack of published studies on their effects. Stump flipping removes the stumps from the plough ridges, where they are left to decompose. Alternatively, the stumps may be removed and used together with ground smoothing resulting in more level conditions for re-establishing bog plants.

1.6.2 Potential carbon gains through restoration

Fenton (2010) estimated 1 ha of peat of 1 m thickness to contain ~1900 t C. However, peat accumulation is a slow process; 0.5 mm yr^{-1} is thought to be a reasonable estimate for northern peatlands (Wieder *et al.*, 1994). Therefore, based on these estimates, peat gains of 0.95 t C ha^{-1} yr^{-1} might be expected if natural bog function is restored. However, Hargreaves *et al.* (2003) and Hommeltenberg *et al.* (2014) suggested carbon losses through accelerated decomposition with afforestation may be between 1 and 3 t C ha^{-1} yr^{-1} from drained spruce forests in Scotland and Germany, respectively. Therefore, the rates of carbon loss through afforestation may outweigh the gains

through subsequent restoration in the short term, but it depends on the time frame of evaluation post-restoration. Since peatlands in the UK have been estimated to contain 20 times more carbon, per hectare, than the average commercial forest plantation (Fenton, 2010), many afforested sites are now being restored in an attempt to recreate functioning bog ecosystems that sequester and store carbon. However, it is still unclear how restoration activity alters the carbon balance in previously afforested bogs.

1.6.3 Impacts of restoration on hydrology and peat properties

Forest-to-bog restoration studies have shown some evidence of a recovery in the peat properties from afforestation effects. Anderson and Peace (2017) speculated that the previously unsaturated peat exhibited renewed buoyancy after re-wetting and clear-felling released overburden pressure, leading to increased peat moisture content and reduced bulk density. However, more information is needed to confirm if this is true. Tree felling has been shown to increase water yield in the short term (Sahin & Hall, 1996), but it is not clear how the hydrological functioning of felled catchments left to rehabilitate, or combined with other restoration methods such as drain and furrow blocking, compare to that of afforested and intact bogs. It could be hypothesised that lower evapotranspiration due to tree removal and functioning drainage systems will lead to greater flow peaks and shorter lag times, but the additional blocking of drains and furrows may attenuate flow. Changes to the peat properties resulting from forest-to-bog restoration, such as hydraulic conductivity, will likely impact subsurface flow. However, more information is needed if the effects of forest-to-bog restoration on peatland ecosystem services are to be fully understood.

1.6.4 Impacts of restoration on water quality

Despite the goal of forest-to-bog restoration to restore pre-afforestation ecosystem function, there have been water quality concerns, particularly after clear-felling. Spikes in phosphorus in porewater and streamwater have been associated with felling operations and linked to the handling of the brash (Asam, 2012; Asam *et al.*, 2014a; Asam *et al.*, 2014b; Clarke *et al.*, 2015; Gaffney *et al.*, 2018; O'Driscoll *et al.*, 2014; Palviainen *et al.*, 2014; Rodgers *et al.*, 2011; Rodgers *et al.*, 2010). Elevated dissolved

organic carbon (DOC) and nutrient concentrations have been observed in streamwater in other clear-felling (Cummins & Farrell, 2003a; Nieminen *et al.*, 2015; Piirainen *et al.*, 2007; Shah & Nisbet, 2019) and restoration (Koskinen *et al.*, 2011; Koskinen *et al.*, 2017; Sallantaus & Koskinen, 2012) studies, although nitrate leaching was less of an issue in ombrotrophic compared to minerotrophic sites (Koskinen *et al.*, 2017).

A rise in phosphorus and DOC concentrations in streams is a particular concern for areas such as the Highlands of Scotland with priority species such as Atlantic salmon (*Salmo salar*), brown trout (*Salmo trutta*), otter (*Lutra lutra*) and the freshwater pearl mussel (*Margaritifera margaritifera*) (BRIG, 2007; Shah & Nisbet, 2019). Ground disturbance and tree debris have also been attributed to the leaching of dissolved metals such as Al, Fe, K and Mn (Asam *et al.*, 2014a; Drinan *et al.*, 2013b; Kaila *et al.*, 2012; Muller & Tankéré-Muller, 2012; Palviainen *et al.*, 2004), which can become toxic to freshwater ecology. Increased acidity and Al concentrations in streamwater have previously been linked to declines in salmon populations (Baker & Schofield, 1982; Harriman *et al.*, 1987), and the freshwater pearl mussel is particularly sensitive to nutrient enrichment (Cosgrove *et al.*, 2017; Strayer, 2014). Elevated DOC, Al, Fe and Mn may also have consequences for drinking water provisions due to the increased costs incurred to water companies for treatment processes in order to keep concentrations below acceptable guidelines (Khadse *et al.*, 2015; WHO, 2011; Williamson *et al.*, 2020)

Strong relationships have been observed between PTEs and DOC concentrations in headwater streams draining organic soils (Chapman *et al.*, 1993) and forest-to-bog studies (Muller *et al.*, 2015; Muller & Tankéré-Muller, 2012) where DOC increases after felling (Gaffney, 2017; Gaffney *et al.*, 2018; Gaffney *et al.*, 2020a; Shah & Nisbet, 2019). The humic substances in DOC form complexes with Al and Fe (Boggs *et al.*, 1985). Mn enrichment is also known to occur with increased DOC from underneath forest stands, but its mobility is thought to be more related to abiotic redox reactions than complexations (Heal, 2001; Heal *et al.*, 2002). Humic and fulvic acids are also thought to form ternary complexes with some metals and oxyanions such as

phosphate with Muller and Tankéré-Muller (2012), suggesting higher DOC concentrations could increase the mobility of both PTEs and phosphorus from the peat to streamwater. Fe (III) complexes with humic substances have been observed to sequester phosphate under the acidic conditions typically found in bogs (Jones *et al.*, 1988; Koenings, 1976; Shaw *et al.*, 1996). The process is also reversible with exposure to light (Jones *et al.*, 1988; Shaw *et al.*, 1996), potentially increasing available levels of phosphorus in streams. However, it is unclear what the dominant processes are from the few forest-to-bog studies that exist.

Chemical fluxes are important for sensitive receiving waters, such as oligotrophic lakes. The accumulation of DOC, nutrients and metals over time may disrupt the balance of aquatic ecosystems leading to eutrophication (Cummins & Farrell, 2003b; Drinan *et al.*, 2013a; Drinan *et al.*, 2013b; Howarth, 2014; RoTAP, 2012) and toxicity to aquatic organisms (Drinan *et al.*, 2013b; Evans *et al.*, 2005; Howarth, 2014). Any increase in the DOC flux (Dawson *et al.*, 2008; Dinsmore *et al.*, 2010; Dyson *et al.*, 2011; Gaffney, 2017; Gaffney *et al.*, 2020a; Qualls *et al.*, 1991; Vinjili, 2012) as a result of forest-to-bog restoration could counteract the intentions of restoring the carbon balance and reducing greenhouse gas emissions (Dinsmore *et al.*, 2010; Drewer *et al.*, 2010; Ojanen *et al.*, 2013; Waddington *et al.*, 2010; Worrall *et al.*, 2003). Fluxes of coloured DOC and particulate organic matter into lakes may also reduce the available light to phytoplankton and macroinvertebrates affecting primary productivity and feeding habits, respectively (Ramchunder *et al.*, 2012). Estimates of aquatic carbon fluxes from intact, afforested, and restored catchments have been made in previous studies, using different calculation methods from catchments with different characteristics (Gaffney *et al.*, 2020a; Vinjili, 2012). However, the very different findings highlight a need for other estimates using comparable methods. Studies that have reported changes in the fluxes of other solutes resulting from forest-to-bog restoration are scarce, although Kaila *et al.* (2014) and Rodgers *et al.* (2010) observed elevated phosphorus fluxes after clear-felling. The accumulation of nutrients and PTEs, particularly after clear-felling, may affect the balance of peatland lakes (Drinan *et al.*, 2013b), leading to eutrophication and oxygen depletion, affecting macroinvertebrate assemblages (Drinan *et al.*, 2013a).

1.6.5 Timescales of recovery after restoration

Although peatland restoration attempts have been ongoing since the 1990s in the UK, it is still unclear whether the aim of restoring afforested peatlands to their former intact state is achievable and what timescales are involved. Some of the earliest forest-to-bog restoration sites in the Flow country (> 17 years) are now thought to behave as carbon sinks (Hambley, 2016), and the corresponding bog chemistry has been found in one study to be similar to near-by pristine bogs (Gaffney, 2017). However, the current thinking is that 20 years is insufficient for a full recovery to a peatland ecosystem with the same plants, animals, and microorganisms (Andersen, 2017; Gaffney, 2017) coexisting as before. The plants needed to restore pre-afforestation ecosystem function and the accumulation of peat have been found to respond well in the initial years after restoration (Jauhiainen *et al.*, 2002; Komulainen *et al.*, 1999; Laine *et al.*, 2011) but have not always continued to re-establish in the years that followed (Anderson & Peace, 2017; Haapalehto *et al.*, 2011; Hancock *et al.*, 2018). Other studies have reported recolonisation by vegetation that is typically associated with intact bog in the first six years, but an absence of some key species thereafter (Anderson & Peace, 2017; Haapalehto *et al.*, 2011; Hancock *et al.*, 2018) is an indication that a complete recovery is not likely to happen quickly.

Some studies have found that the damming of both drainage ditches and ploughed furrows leads to water-table levels recovering towards those observed in intact bogs and the ground's surface to rise after restoration (Anderson & Peace, 2017; Muller *et al.*, 2015). However, Gaffney *et al.* (2020b) found that damming drainage ditches alone resulted in a very localised impact on water-table levels, suggesting that blocking furrows may also be necessary to raise water tables over whole forest blocks. However, water-table recovery may not necessarily indicate a recovery of hydrological function if other peat properties remain in conditions similar to afforested systems. The possibility that the restoration may transform landscapes into habitats significantly different from intact bogs may mean new techniques are necessary.

1.7 Knowledge gaps

Of the few studies that have looked at forest-to-bog restoration (Anderson, 2017; Gaffney et al., 2020a; Hambley, 2016; Muller et al., 2015; Shah & Nisbet, 2019), most have been on blanket peatlands and the impact on streamwater solute concentrations. Despite their importance in controlling the carbon balance and solute fluxes, there is limited information on how the hydrological functioning and peat properties respond following forest-to-bog restoration. No studies have looked at how peat properties, such as hydraulic conductivity, are affected by forest-to-bog restoration and how this affects the peatland's hydrology and the downstream river regime. Anderson et al. (2000) studied the initial impact of plantation forestry on streamflow in the first five years following drainage and planting, but the control used in their study had also been drained, making comparisons with intact bogs difficult. The most comprehensive long-term study into flood risk from afforested peatland catchments in the UK (Bathurst et al., 2018; Birkinshaw et al., 2014; Robinson, 1998) found forestry drainage to initially reduce peak lag times, but these gradually recovered to pre-drainage values as drains infilled with tree litter and the trees matured. However, there is an absence of studies on how the water balance, river flow regime and response to storm events respond to forest-to-bog restoration, affecting the flux of solutes to streams draining these catchments.

Furthermore, it is unclear whether raised bogs respond to restoration in the same way as blanket bogs. Water-table recovery has been reported in UK blanket peatlands after forest-to-bog restoration (Anderson & Peace, 2017; Gaffney et al., 2018; Muller et al., 2015), but similar studies for raised bogs are currently limited to Fennoscandia (Haapalehto et al., 2014; Haapalehto et al., 2011; Komulainen et al., 1999; Koskinen et al., 2011; Laine et al., 2011; Menberu et al., 2016), and the trees were not always felled, making comparisons difficult. Aquatic carbon, nutrient, and PTE fluxes will be influenced by changes in nutrient cycling within the plant-peat system and flow pathways and hydrological fluxes, and further work is required to establish the impacts of forest-to-bog restoration. There is still uncertainty about the origin of some of the elevated nutrient concentrations in surface waters after forest-to-bog restoration and the processes involved. Much of the surface water nutrient enrichment has been attributed

to their release from decomposing forest residues (Asam *et al.*, 2014b). However, more information is needed on factors controlling nutrient transport from source to streams to assess restoration management practices. The different restoration processes will affect how the restored peatlands function and clearer evidence is needed to provide cost-effective solutions to minimise the environmental impacts of forest-to-bog restoration.

1.8 Research questions and approach

1.8.1 Key questions

Given the paucity of forest-to-bog studies and the research gaps previously identified (Figure 1-5), the overall aim of this research project was to determine how the physical and chemical properties of peat, hydrology and hydrochemistry of porewater and streamwater differ between intact, afforested and forest-to-bog restoration sites on both blanket and raised bogs. As such, the thesis is based on four main research questions and a further cross-cutting question, as follows:

1. How do peat physical and chemical properties differ between intact, afforested and restored raised bogs and blanket bogs?

2. How does porewater chemistry differ between intact, afforested and restored raised bogs and blanket bogs?

3. How does hydrological functioning differ between intact, afforested and restored raised bogs and blanket bogs?

4. How do streamwater chemistry and chemical fluxes differ between intact, afforested and restored raised bogs and blanket bogs?

5. What are the implications of environmental responses to forest-to-bog restoration for site managers and policy development?

The four main research questions are addressed in chapters 2 - 5 and discussed further in a final synthesis of the findings (Chapter 6). Question 5 is considered in each of the main research chapters and the final synthesis chapter.

1.8.2 Research approach

This research will complement current monitoring by Forest Research (as the sponsor of the project) into the effects of forest-to-bog restoration work on water quality in Scotland by comparing differences between afforested catchments and those that have undergone forest-bog restoration or are near-natural (hereafter referred to as intact). An observational approach was used to address the research questions by taking measurements and samples from the field. There were three main treatments in all studies: intact, afforested, and restored bog (sites) and two types of bog – blanket and raised from different locations in Scotland. However, the forest-to-bog restoration sites were of different ages, and different tree-felling and restoration practices had been carried out at each site. Question 1 was addressed by taking soil cores from the three treatments from two raised bog and two blanket bog locations from one point in time. Laboratory analysis determined any differences in the physical and chemical peat properties between the three main treatments, locations, and peatland type. Questions 2 - 4 were addressed by an 18-month study that continuously monitored rainfall, water table and streamflow and collected samples of porewater and streamwater at regular intervals from two locations – a raised bog and a blanket bog that contained mini-catchments of the three treatments. Question 2 was addressed by sampling peat porewater, which was analysed in the laboratory to assess differences in soluble carbon and nutrient concentrations between the treatments, sites and locations. Question 3 used the continuous water table, streamflow, and rainfall data to assess hydrological functioning differences between treatments, sites, and locations. Question 4 was addressed by taking streamwater samples to determine differences in soluble carbon, nutrient and PTE concentrations, and fluxes between the three treatments, sites, and locations.

1.8.3 Study locations and sites

Examples of intact, afforested, and restored bogs were selected from different raised bog and blanket bogs locations in Scotland. Two raised bog locations and two blanket bog locations were used for Question 1. Questions 2 - 4 used the same two locations: one raised bog (Flanders Moss) and one blanket bog (Forsinain). A summary of the sites is given in Table 1-2 and their locations in Figure 1-10. The two Flow Country locations are within the RSPB Forsinard Flows National Nature Reserve in Caithness and Sutherland. Flanders Moss is one of a series of lowland raised bogs in the Carse of Stirling. The Forestry Commission manages Flanders Moss West and Flanders Moss National Nature Reserve to the east is managed by NatureScot (formerly Scottish Natural Heritage) and remains largely intact. Ironhirst Moss is part of the North Solway mosses in Dumfries and Galloway. At each location, sites of intact, afforested, and restored bog were selected. The intact sites were as close to near-natural bog as could be found, and the afforested bogs were planted with a mixture of Sitka spruce (*Picea sitchensis*) and lodgepole pine (*Pinus contorta*) with near 100% closed canopy cover. The vegetation in the intact bogs was a similar mixture of sedges, reeds, ericaceous shrubs, sundews, and *Sphagnum* mosses with bogbeans and bog myrtle, and liverworts at the Flow Country locations. The restored sites at Flanders Moss had been clear-felled, but other restoration measures had not yet taken place at the time of the study. At Forsinain, the restoration sites had been clear-felled and drain- and furrow-blocking had taken place shortly after felling and in March 2019. All locations had minimum peat depths greater than 1 m, and the underlying geology was sedimentary. More detailed descriptions of the sites are given in the proceeding chapters.

Table 1-2 – Study areas used to address the four main research questions (Q1 - Q4).

Location	Bog classification	Research Questions	Region	Lat/lon
Flanders Moss	Raised bog	Q1,Q2,Q3,Q4	Stirlingshire	56°09'47.4"N 4°10'54.0"W
Forsinain	Blanket bog	Q1,Q2,Q3,Q4	Flow Country	58°25'15.9"N 3°51'42.6"W
Ironhirst Moss	Raised bog	Q1	Dumfries and Galloway	55°01'36.8"N 3°30'01.1"W
Talaheel	Blanket bog	Q1	Flow Country	58°24'39.9"N 3°48'09.6"W
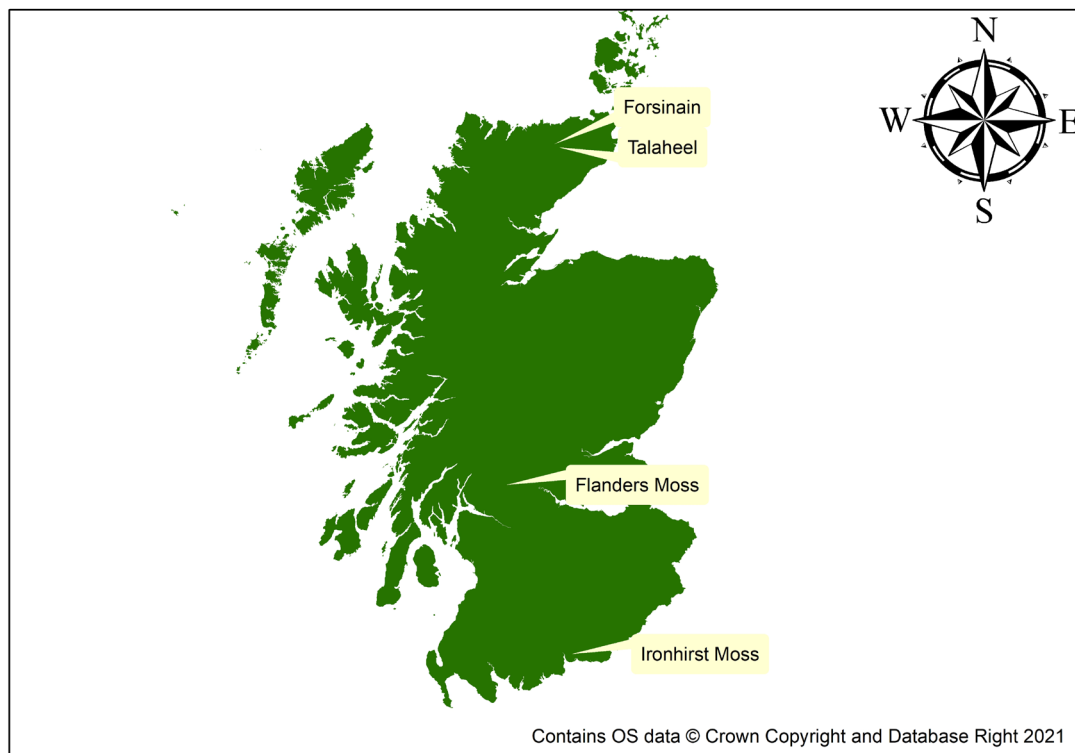
Figure 1-10 – Map of Scotland showing the locations of the different study areas.

1.8.4 Research methodology

Question 1 was addressed via a stratified random sampling procedure to take peat cores from different microforms associated with intact, afforested and raised bogs. Common physical and chemical properties, including bulk density, moisture content, loss on ignition, specific yield (Price, 1996), von Post humification, pH and electrical conductivity, were analysed under laboratory conditions. Also, field measurements of hydraulic conductivity were taken using a combination of piezometer slug (Baird *et al.*, 2004) and tension infiltrometer tests (Holden, 2009; Zhang, 1997). Question 2 was approached by sampling porewater and water-table depth at regular intervals from piezometer-dipwell nests at four different depths over 18 months from two locations. Samples were analysed at the University of Leeds laboratories for pH, electrical conductivity, DOC and dissolved nutrients. The porewater samples were also measured for spectral absorption, and the E4:E6 and $SUVA_{254}$ were calculated to estimate DOC aromaticity. Question 3 was addressed using pressure transducers to record water levels in dipwells and streams at 15-minute intervals over the same 18-month period supplemented by manual water-table sampling to cover a wider spatial range. Rainfall

was recorded by tipping bucket rain gauges and in-situ data loggers. The stream stage heights, in conjunction with V-notch weirs, were used to form stage-discharge relationships. Addressing Question 4 involved regular streamwater sampling and analysis for pH, electrical conductivity, alkalinity, DOC, total and dissolved nutrients (N and P), base cations, and total and dissolved PTEs (Al, Fe and Mn).

1.8.5 Thesis outline

This thesis consists of the research results from four manuscripts and ends with a synthesis of the main findings. A summary of the chapters is given below:

Chapter 2: A comparison of peat properties in intact, afforested and restored raised and blanket bogs.

The peat's common physical and chemical properties were compared between four locations of intact, afforested and restored raised bog and blanket bog sites. A random stratified sampling procedure was used to take peat cores from different microforms at two raised bog and blanket bog locations where forest-to-bog restoration had taken place.

Chapter 3: A comparison of porewater chemistry between intact, afforested and restored raised and blanket bogs.

DOC and nutrient concentrations in peat porewater were compared between intact, afforested and restored raised bog and blanket bog locations over 18 months. Porewater was sampled from intact, afforested and two forest-to-bog restoration sites at both a raised bog and a blanket bog location. The pH, electrical conductivity, DOC and nutrient concentrations of the porewater at the restoration sites were compared to the porewater chemistry at the intact and the afforested sites.

Chapter 4: The effect of forest-to-bog restoration on the hydrological functioning of raised and blanket bogs.

The hydrological functioning of intact, afforested, and restored raised bog and blanket bog sites was compared over 18 months. High temporal resolution streamflow and

water-table depth measurements were taken from the same sites used in Chapter 3. Additional rainfall and temperature data were used in the assessment of the streamflow, water-table dynamics, and water balance from each of the catchments.

Chapter 5: The effect of forest clearance for peatland restoration on streamwater quality and fluxes of dissolved organic carbon, nutrients, and potentially toxic elements.

Solute concentrations and fluxes from streams draining intact, afforested, and restored raised bog and blanket bog sites were compared over 18 months at the same sites as Chapters 3 and 4. Streamwater was sampled monthly when water was flowing and analysed for soluble carbon, nutrients, base cations, and potentially toxic elements. Discharge data from Chapter 4 were used to calculate solute fluxes for soluble carbon, nutrients and potentially toxic elements presented in Chapter 5.

Chapter 6: Synthesis

Chapter 6 synthesises the main findings presented in this thesis, drawing together Chapters 2 – 5 and discussing their wider implications. The limitations of the study and directions for future work are also discussed. The chapter ends with a summary of the conclusions from the thesis.

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Chapter 2: A comparison of peat properties in intact, afforested and restored raised and blanket bogs

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Abstract

Recognition of peatlands as a key natural store of terrestrial carbon has led to new initiatives to protect and restore them. Bogs subjected to plantation forestry are now being clear-felled and restored (forest-to-bog restoration) to recover pre-afforestation ecosystem function. However, little is known about differences in peat properties between intact, afforested and restored bogs. A stratified random sampling procedure was used to take 122 peat cores from three separate microforms associated with intact (hollows; hummocks; lawns), afforested and restored bogs (furrows; original surface; ridges) at two raised and two blanket bog locations. Common physical and chemical properties of the peat were measured in the laboratory at eight separate depth increments. Bulk density was significantly higher and moisture and carbon content slightly lower in the afforested (means = 0.103 g cm^{-3}, 87.8% and 50.9%, respectively) than the intact (means = 0.091 g cm^{-3}, 90.3% and 51.3%, respectively) and restored bogs (means = 0.095 g cm^{-3}, 89.7% and 51.1%, respectively). The pH was significantly lower in the afforested (mean = 4.26) and restored bogs (mean = 4.29) than the intact bogs (mean = 4.39), whereas electrical conductivity was significantly higher (means: afforested = 34.2, restored = 38.0, intact = 25.3 μS cm^{-1}). No significant differences were observed in the peat properties between intact bog microforms, but there were significant differences in humification, specific yield and carbon content between afforested bog microforms in the top 60 cm of peat. Our results show that despite significant differences in peat properties between treatments, effect sizes were mainly small and greater natural differences in pH, electrical conductivity, specific yield, and saturated hydraulic conductivity existed between the different intact bogs. Therefore,

natural variability between locations and peatland type must be considered when interpreting land management impacts on peatland properties and functioning.

2.1 Introduction

A third of global soil carbon is thought to be stored in peatlands (Scharlemann *et al.*, 2014; Yu *et al.*, 2010), but their ability to act as carbon sinks depends on their condition. Worldwide, 12% of peatlands are degraded and potentially act as a carbon source to the atmosphere (Joosten, 2016). Continued global industrial development has led to the loss of former peat accumulating landscapes through land management and climate change. In particular, afforestation has led to significant peatland habitat loss worldwide with the planting of non-native species on treeless or naturally forested peatlands for timber (Anderson *et al.*, 2016; Strack, 2008) or palm oil production (Joosten *et al.*, 2016; Sangok *et al.*, 2017). Palviainen *et al.* (2004) estimated 15 million hectares of natural peatlands had been drained for forestry worldwide. Up to 600 000 ha (Cannell *et al.*, 1993; Paavilainen & Päivänen, 1995) of UK peatlands may have been drained for forestry, with 9% of the total area of deep peat planted with coniferous trees between the 1950s and 1980s (Cannell *et al.*, 1993; Hargreaves *et al.*, 2003).

There has been considerable investment in restoration initiatives following interest in the carbon storage potential of peatlands and wider ecosystem service benefits (Anderson, 2001; Anderson *et al.*, 2016). Forest-to-bog restoration is one example, where trees are felled and drains blocked to raise the water table in an attempt to restore peatland functions (Anderson, 2001; Anderson & Peace, 2017; Gaffney, 2017; Gaffney *et al.*, 2018; Muller *et al.*, 2015; Muller & Tankéré-Muller, 2012; Shah & Nisbet, 2019). Forestry on peatlands lowers the water table due to drainage and increased evapotranspiration from growing tree stands (Anderson, 2001). Felling has been found to reverse this process to a degree, but the blocking of drains and furrows is usually required to restore water-table levels to those of intact bogs (Anderson & Peace, 2017; Howson *et al.*, 2021a; Koskinen *et al.*, 2011; Koskinen *et al.*, 2017; Menberu *et al.*, 2016). However, little is known about the effects on peat properties following prolonged water-table draw-down associated with plantation forestry or

restoration after felling. Post-drainage consolidation of the peat, shrinkage of dried peat near the surface and wastage through oxidation after drainage, compaction from the weight of the trees (Anderson & Peace, 2017; Liu *et al.*, 2020) and the presence of tree roots may mean that the properties of peat several years after restoration are still significantly different to those found in intact systems.

The effects of afforestation on peat properties are difficult to predict since there are several interacting factors. Compression from the weight of the trees may be expected to increase bulk density and decrease hydraulic conductivity as soil pores collapse (Silins & Rothwell, 1998). Alternatively, the top layers of drying peat may experience desiccation cracks, increasing hydraulic conductivity (Holden *et al.*, 2004). Such changes may also have implications for the peat's water storage capacity (Price & Schlotzhauer, 1999) and carbon content (Simola *et al.*, 2012). Higher bulk densities, reduced moisture content and subsidence have been attributed to peat compression and oxidation, but the magnitude of change in each property is unclear (Anderson & Peace, 2017; Price & Schlotzhauer, 1999; Sloan *et al.*, 2019). Oxidation of surface peat also leads to greater humification and loss of carbon to the atmosphere. Mustamo *et al.* (2016) found that hydraulic conductivity, bulk density, and humification were strongly co-dependent, but they suggested considerable spatial variability could be due to the dominance of macropores (Wallage & Holden, 2011). A study on tropical peatlands found reduced soil carbon concentrations in mature palm oil plantations compared to near-natural peat swamp forests (Tonks *et al.*, 2017). Simola *et al.* (2012) estimated forestry drained peatlands in Finland to be losing 1.5 t C ha^{-1} yr^{-1} after analysing peat cores taken from 37 different locations previously sampled in the 1980s. Hargreaves *et al.* (2003) recorded similar rates of C loss, 1 t C ha^{-1} yr^{-1}, for a closed-canopy forest on drained peat in Scotland using eddy covariance flux measurements. In contrast, Hommeltenberg *et al.* (2014) estimated higher rates of C loss, 3 t C ha^{-1} yr^{-1}, from a peatland spruce plantation in Germany, but their estimate relied on the assumption that 50% of peat volume loss due to subsidence was oxidative wastage. However, studies on how the afforestation of peatlands affects the peat carbon stock are scarce.

Anderson and Peace (2017) found an apparent recovery in blanket peat bulk density and moisture content 10 years after clear-felling and blocking furrows. As a result, a limited reversal in subsidence was observed, suggesting that some peat mass swelling can occur in response to restoration. In turn, this swelling may increase the peat permeability as pore spaces open up, but studies to assess this hypothesised mechanism have never been undertaken. We could not identify other studies that have looked at forest-to-bog restoration effects on peat properties. Studies from peatlands restored after severe disturbances such as peat harvesting (Price, 1996; Price & Schlotzhauer, 1999) may offer insights into potential forest-to-bog impacts on peat properties, but further work is required to establish whether such findings apply to restoration after forestry operations. Studies on previously harvested peatlands in Quebec (González *et al.*, 2014; McCarter & Price, 2015; Price, 1996; Price & Schlotzhauer, 1999) found spontaneous recolonised vegetation in abandoned sites and a shift towards wetland favouring species 3-17 years after restoration. However, where restoration had allowed for the regeneration of *Sphagnum* mosses, the difference in physical properties of the surface layers and the underlying peat often meant near-natural peatland function did not return in the short term. McCarter and Price (2015) concluded additional structural growth, decomposition and consolidation of the regenerated *Sphagnum* would be necessary before previously harvested bog would return to a favourable status. Given the lack of forest-to-bog studies on peat properties, our main aim was to quantify common physical and chemical characteristics to determine differences between intact, afforested, and restored bogs. We hypothesised that the peat properties in the afforested bogs would significantly differ from those found in intact systems, but the properties in forest-to-bog restoration sites would lie somewhere between those found in afforested and intact bogs.

2.2 Methods

2.2.1 Study Sites

The sites were chosen from two raised bog and two blanket bog locations in Scotland, each containing areas of undisturbed peatland (hereafter referred to as intact bog), forestry (hereafter referred to as afforested bog), and forest-to-bog restoration of different ages (hereafter referred to as restored bog). The two blanket bog locations,

Forsinain and Talaheel, were situated in the RSPB Forsinard Flows National Nature Reserve, northern Scotland (Figure A1-1). The reserve is part of the Flow Country which is Europe's largest expanse of blanket bog. The raised bog locations were in central and southern Scotland (Figure A1-1), one at Flanders Moss, which is part of a series of lowland raised bogs formed on the uplifted former estuary of the River Forth, and the second at Ironhirst Moss, part of the North Solway Mosses, Dumfries. Examples of intact bog, first rotation afforested bog and restored bog were selected for taking peat cores at each location where peat depths were greater than 1 m. Table 2-1 provides further characteristics of the chosen sites at each location.

Table 2-1 – Characteristics of chosen sites

Location	Site	Description	Bog classification	Region	Lat/Lon	Mean Peat depth (m)	Planting dates	Felling dates	Coring dates
Forsinain	FOAB	Afforested bog	Blanket bog	Flow Country	58°25'30.6"N 3°52'08.0"W	2.3	1980		16/12/2018
	FOIB	Intact bog			58°25'15.9"N 3°51'42.6"W				06/08/2019
	FOR1	Old Restored			58°26'01.3"N 3°51'21.3"W		1980	2002/03	06/08/2019
	FOR2	Young Restored			58°25'30.0"N 3°51'46.4"W		1980	2014/15	16/12/2018
Talaheel	TAAB	Afforested bog	Blanket bog	Flow Country	58°24'02.8"N 3°48'33.2"W	2.3	1981		26/09/2019
	TAIB	Intact bog			58°24'39.9"N 3°48'09.6"W				25/09/2019
	TAR1	Restored			58°24'46.6"N 3°48'22.2"W		1981	1997/98	25/09/2019
Flanders Moss	FMAB	Afforested bog	Raised bog	Stirlingshire	56°09'07.1"N 4°19'53.5"W	4.5	1965		25/06/2019
	FMIB	Intact bog			56°09'47.4"N 4°10'54.0"W				25/06/2019
	FMR1	Old Restored			56°08'07.9"N 4°19'26.1"W		1965	24/11/2009 - 09/12/2009 01/08/2011 - 18/10/2011	13/12/2019
	FMR2	Young Restored			56°08'26.5"N 4°19'25.2"W		1965	01/10/2013 - 31/03/2014	13/12/2019
Ironhirst Moss	IRAB	Afforested bog	Raised bog	Dumfries and Galloway	55°01'38.3"N 3°30'00.7"W	5.0	2005		14/11/2019
	IRIB	Intact bog*			55°01'36.8"N 3°30'01.1"W				14/11/2019
	IRR1	Restored			55°01'20.5"N 3°29'35.9"W		1971	1999/00	14/11/2019

* - Due to site restrictions, intact cores were taken from a wide, unplanted gap in the forest.

Nearby sites of intact, afforested and restored bog were selected at each location where peat depths exceeded 1 m. The different locations represent blanket bog and raised bogs typically found in the UK and classified as deep peat. The intact sites were the closest we could find to pristine bogs at each location and were largely assessed by the abundance of *Sphagnum* mosses and other characteristic bog plants, including sedges, ericaceous shrubs, sundews (*Drosera spp.*), bog asphodel (*Narthecium ossifragum*), bog myrtle (*Myrica gale*) and bogbean (*Menyanthes trifoliata*) in natural pools. At the time of planting, the afforested bogs had been planted to standard UK forestry guidelines, with the same mixture of Sitka spruce (*Picea sitchensis*) and lodgepole pine (*Pinus contorta*) and were largely closed canopy at the time of the study. The restored bogs were felled at different times, and restoration methods differed, but any standing trees had been removed, and no further ground smoothing had been carried out. Therefore, surface conditions were similar between the restored sites, and they can be deemed reasonably representative of forest-to-bog restoration sites where the afforested microforms are still visible. At Ironhirst Moss and Flanders Moss, the first rotation forest was felled and not restocked, and no additional restoration was carried out, although drain blocking and other re-wetting treatments are scheduled for the latter. Brash was either removed and chipped for biomass, left on site to decompose, or compressed into furrows and drains. The trees were mulched from standing at the youngest restoration site at Forsinain, using a mechanical masticator, and the woodchips spread on the peat surface. At Forsinain and Talaheel, drain and furrow blocking had also taken place.

2.2.2 Sample collection

A random stratified sampling procedure (Figure 2-1) was adopted where 60 x 60 m grids were selected at each site, and three individual 10 x 10 m cells were selected at random for obtaining peat cores. In each cell, cores were taken from three different microforms: hollows, hummocks and lawns in the intact bogs, and ridges, furrows and the area between furrows and ridges (hereafter referred to as the original surface) in afforested and restoration sites. Therefore, nine peat cores were taken from each site using a Russian corer, and each core's location was recorded using GPS. Each peat core was placed in a 1 m section of PVC guttering for protection and wrapped with

cellophane to form an airtight seal. On return to the laboratory, the cores were refrigerated at 4 °C before analysis, usually within a month of collection. 122 peat cores were taken from the 126 selected cells. It was impossible to take three cores from the afforested Talaheel site and one core from the afforested Ironhirst Moss site where the peat was most compressed, and damage was sustained to the Russian corer. Cores were not taken in drought periods, and conditions were similar at the time of sampling. Therefore, the water-table position would have been similar between sampling times and there would have been little difference in peat saturation of the 1 m deep cores for each treatment.

INTACT   AFFORESTED   RESTORED
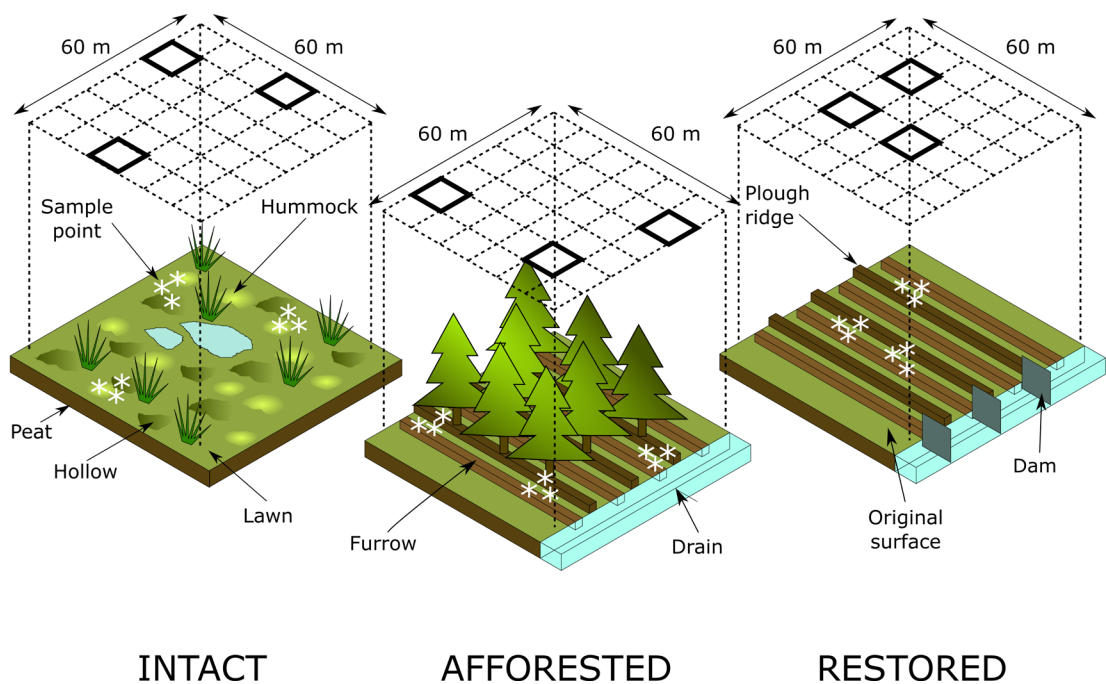
Figure 2-1 – Stratified random sampling procedure for peat core selection at each site – Three 10 x 10 m grid squares were selected at random, and three 1 m cores were taken from the different microforms in each (Intact: hummocks, hollows, lawns; Afforested and restored: furrows, ridges and the original surface).

2.2.3 Laboratory analysis of peat

Peat cores were generally analysed in batches of nine over a week, usually within a month after collection. Each peat core was split into eight depths (0-10, 10-20, 20-30, 30-40, 40-50, 50-60, 60-80, 80-100 cm) for subsequent analysis. A 32 mm diameter cylindrical cutter was used to take a subsample of peat from each section's deepest end. The remaining peat was then placed in airtight bags, labelled, and returned to refrigerated storage between analyses. The subsamples were weighed along with a muslin cloth square, used to wrap the sample to prevent any peat loss when measuring

specific yield (S_y). The muslin cloth square was held in place by elastic bands to form a parcel of peat. Samples were placed in a tank of rainwater and allowed to soak for 24 hours. They were then weighed and placed on a sieve, covered with a lid, and allowed to drain for 24 hours before reweighing. An estimate of S_y was calculated using Price's (1996) method, which is determined as the difference in saturated and drained peat weights divided by the saturated weight. A correction factor was used to account for the water absorbed by the muslin cloth from a regression relationship between the dry and wet weights of the muslin cloth per gram after soaking for 24 hours, followed by draining for 24 hours.

After calculating S_y, the samples were transferred to crucibles, making sure not to lose any peat, and oven-dried at 105 °C until they were at a constant weight. The oven-dried weights were recorded for each sample before being placed in a muffle furnace for 16 hours at 550 °C. After cooling in a desiccator, the remaining ash was weighed to determine the loss of organic matter. The bulk density was calculated from the oven-dried mass divided by the sample's initial volume. Moisture content was determined from the difference in weight between the fresh and oven-dried sample divided by the fresh sample weight. Loss on ignition was calculated from Equation 1

$$\%LOI = \left(\frac{oven\ dried\ mass\ (g) - ashed\ mass(g)}{over\ dried\ mass\ (g)} \right) \times 100 \qquad (1)$$

where %LOI is percentage loss on ignition, equivalent to the percentage of organic matter with a 0.05% detection limit; the balances had an accuracy of 0.04g and were calibrated between weighing batches of samples.

Peat acidity and electrical conductivity were determined by measuring pH and conductivity in a suspension of fresh peat in deionised water at a 1:10 ratio of wet peat mass to solution (Rowell, 1994) using a HANNA 9124 pH meter and a HORIBA B-173 conductivity meter, both with automatic temperature compensation. Before batches

of readings, two-point calibration was used to calibrate the pH probe using buffer solutions of 4 and 7 pH units. The conductivity meter was calibrated by first soaking the sample well with deionised water and then using a 1.41 mS cm^{-1} calibration solution. The conductivity probe well was rinsed with deionised water and dried with tissue paper to prevent dilution readings. The peat-water mixture was stirred and then placed on a shaking table for 1 hour before taking pH and electrical conductivity. The humification of each sample was assessed by squeezing the peat, and the amount of amorphous material that passes through the fingers, plant remains, and the colour of the expelled water, if any, were used to estimate the degree of humification on the 10-point von Post scale (von Post, 1922).

The percentage carbon content (hereafter referred to as carbon content) was determined from the loss on ignition and the regression of Bol *et al.* (1999) used by Garnett *et al.* (2001) and Parry and Charman (2013) for moorland soils, which included deep peat. Carbon content was calculated from the regression given by Equation 2

$$\%C = (\%OM \times 0.526) - 0.167 \qquad (2)$$

where *%C* is the percentage carbon content of the sample and *%OM* is the percentage organic matter content determined by loss-on-ignition.

Carbon density was calculated by multiplying the carbon content, as a fraction, by the dry bulk density for each sample. The result was then multiplied by the depth increment to give the carbon weight per unit area. However, it is impossible to compare the carbon stock between the sites as the peat in the afforested sites has experienced peat volume changes due to shrinkage and compression (Price & Schlotzhauer, 1999). Also, oxidative wastage can lead to significant subsidence after drainage and afforestation (Anderson & Peace, 2017; Shotbolt *et al.*, 1998; Sloan *et al.*, 2019), resulting in a lowering of the peat's surface by 40 - 80 cm, 30 - 50 years after forest

ploughing and planting (Shotbolt *et al.*, 1998; Sloan *et al.*, 2019). Subsidence over time would mean the sampled peat would not be the same as the original peat before drainage and afforestation. Also, changes in bulk density through compression make calculations impossible because the degree of oxidative wastage and compression are not known. Therefore, this study only presents carbon content (% C) and carbon density (g C cm^{-3}).

2.2.4 Field tests

Saturated hydraulic conductivity (K_s) was measured in the field, at Flanders Moss and Forsinain, using a combination of piezometer slug tests (Baird *et al.*, 2008; Baird *et al.*, 2004; Surridge *et al.*, 2005) where water tables were shallow, and mini-disc tension infiltrometer tests where water tables were drawn down (Zhang *et al.*, 2016). Infiltrometer tests were performed at three locations in each site ($n = 6$) at 20 and 40 cm depths. All the piezometers had an inner diameter of 2.9 cm and 10 cm intakes precisely machined, so they were comparable. The slug tests were conducted at 20 ± 5 cm and 40 ± 5 cm depths. A hole was augured in the peat to the piezometer diameter, and the piezometers were inserted into the hole with an internal cylindrical blocker held in place over the intake screen to prevent peat entry on insertion. Once the piezometers were at the correct depth, the blockers were removed, and they were developed to remove any peat that may be obscuring the intakes. The piezometers were developed by removing all the water with a dosing syringe and then leaving them to refill. Once refilled, enough water was sampled to test for particulates. The process was repeated until the water was not cloudy, indicating any peat obscuring the intakes had been removed. Level-Troll 500 pressure transducers were inserted into the piezometers, and the water level was allowed to stabilise. Slug tests at 20 and 40 cm depths were carried out by adding 30 mL of water with the dosing syringe, and the piezometers were left to refill until the water was at the resting level. Throughout the process, the pressure transducers recorded the water level every 5 seconds. Additional slug tests were carried out at 60 and 80 cm depths at some sites where 30 mL of water was removed from the piezometers. K_s for the piezometer slug tests was calculated using the Hvorslev (1951) equation given by Equation 3

$$K_s = -\frac{A}{Ft} log_e \left(\frac{h}{h_0}\right) \tag{3}$$

where A is the inside cross-sectional area of the piezometer, F is the shape factor of the piezometer, t is time, h is the difference in head between the piezometer and the soil around the intake, and h_0 is the initial head difference.

In forestry sites, where the water table was drawn down, and piezometer tests could not function, METER group mini-disc infiltrometers (Holden, 2009; Holden *et al.*, 2001; Zhang *et al.*, 2016) were used to estimate K_s. Peat was exposed or carefully excavated using a trowel for 0 cm, 20 cm and 40 cm depths and a fine layer of moist sand spread between the disc and the peat. A suction head of -0.5 cm was used since it was the closest attainable to zero. Three measurements were taken from 0, 20, and 40 cm depths from afforested sites and additional surface measurements from one restoration site. The van Genuchten alpha value for the peat and the suction head were used to calculate other van Genuchten soil parameters from the van Genuchten equation (van Genuchten, 1980). The alpha value was estimated from the relationship between bulk density and organic matter content for *Sphagnum* peat (Liu & Lennartz, 2019). K_s was calculated by dividing C_1 (the slope of cumulative infiltration (cm) against the square root of time (s)) by A (Zhang, 1997). A related to the van Genuchten values for the peat at the given suction and radius of the infiltrometer disc as calculated by the van Genuchten equation for the given alpha value (van Genuchten, 1980).

2.2.5 Data analysis

The distributions of peat property variables were tested in Minitab (Minitab 19 Statistical Software, 2020), and where normality and homogeneity of variance were found, any significant differences were determined from one-way ANOVA tests followed by *post-hoc* analysis. Non-parametric tests were performed using Kruskal-Wallis and pairwise comparisons in SPSS (IBM Corp., 2016). The effect size was calculated using rstatix (Kassambara, 2020) in R Studio (RStudio-Team, 2016). Eta squared (η^2) was calculated for one-way ANOVA tests, whereas the effect size for non-

parametric tests (r) was calculated from the Z statistic divided by the square root of the sample size (N). Mann Whitney-U tests were used to test differences between the two bog classifications (raised bog; blanket bog). Spearman's rank correlation coefficients (r_s) were calculated for testing relationships between variables. Variables were plotted for the different treatments and sites over the depth profile using ggplot 2 (Wickham, 2016) in R Studio. Descriptive statistics were calculated in SPSS and Minitab. Differences between the three main treatments (intact, afforested, restored) were first tested, followed by differences between bog type, location and microtopographic levels. Statistical analyses were also performed on the different methodologies used for hydraulic conductivity measurements.

2.3 Results

2.3.1 Differences in peat properties between treatments

2.3.1.1 Entire core

Bulk density was significantly higher in afforested bogs than in both the intact and restored bogs ($p < 0.05$, Kruskal-Wallis, $r > 0.07$) (Figure 2-2). However, bulk density in the intact and restored bogs was not significantly different at the 95% confidence interval ($p = 0.063$, Kruskal-Wallis). Moisture content was significantly different between all three treatments ($p < 0.001$, Kruskal-Wallis, $r > 0.10$), lowest in afforested and highest in intact bogs. Carbon content was significantly lower in afforested and highest in intact bogs ($p < 0.001$, Kruskal-Wallis, $r > 0.30$). Carbon density was significantly higher in the afforested bogs ($p < 0.05$, Kruskal-Wallis, $r > 0.08$), where the bulk density was significantly higher than the other treatments. While the mean S_y was lowest in intact and highest in restored bogs (Table 2-2), there were no significant differences between the three treatments ($p = 0.497$). The pH was significantly higher in the intact than in the afforested and restored bogs ($p < 0.005$, one-way ANOVA, $\eta^2 > 0.02$), while electrical conductivity was significantly lower in the intact bogs ($p < 0.01$, Kruskal-Wallis, $r > 0.4$). However, no significant difference was observed between afforested and restored bogs for pH ($p = 0.460$, one-way ANOVA) and electrical conductivity ($p = 0.850$, Kruskal-Wallis), respectively. The geometric mean of K_s was 1.7×10^{-4} cm s^{-1} across all sampled depths, but no significant difference was observed between treatments ($p = 0.616$, Kruskal-Wallis).

Table 2-2 – Descriptive statistics for the three main treatments for all measured variables over the whole 1 m peat core. CLD = compact letter display (the same letters signify no significant difference between the treatments at the 95% confidence interval); N = sample size; SE = standard error of the mean; von Post estimates are given as 1 – 10 for the degree of humification. EC = electrical conductivity.

Variable	Type	CLD	N	Mean	SE	Min	Median	Max
Bulk density (g cm^{-3})	AB	a	256	0.1034	0.0026	0.0091	0.0959	0.2500
	IB	b	286	0.0913	0.0015	0.0147	0.0883	0.2038
	R	b	422	0.0952	0.0013	0.0323	0.0921	0.2729
Moisture (%)	AB	a	257	87.75	0.39	32.89	89.15	98.56
	IB	b	286	90.30	0.16	78.87	90.58	98.44
	R	c	422	89.70	0.14	64.14	90.05	96.67
C (% of dry mass)	AB	a	248	50.899	0.079	44.132	51.224	52.407
	IB	b	282	51.263	0.082	37.185	51.574	52.411
	R	c	405	51.120	0.073	35.894	51.415	52.369
S_y	AB	a	257	0.0827	0.0028	0.0036	0.0749	0.3432
	IB	a	286	0.0778	0.0022	0.0055	0.0738	0.2425
	R	a	422	0.0871	0.0030	0.0033	0.0745	0.6093
von Post	AB	a	257	5.6	0.099	1.1	5.4	9.5
	IB	b	286	6.0	0.101	1.1	6.3	9.5
	R	ab	423	5.9	0.078	1.1	6.2	9.4
pH	AB	a	257	4.26	0.026	3.54	4.16	5.64
	IB	b	286	4.39	0.020	3.53	4.39	5.10
	R	a	423	4.29	0.014	3.38	4.30	5.15
EC (μS cm^{-1})	AB	a	257	34.21	1.36	11	31	280
	IB	b	286	25.26	1.47	11	21	350
	R	a	423	38.01	1.75	12	31	330
Infiltrometer K_s (cm s^{-1})	AB	a	18	0.001317	0.000226	0.000001	0.001421	0.002634
	R	a	3	0.001876	0.000403	0.001381	0.001572	0.002674
Piezometer K_s (cm s^{-1})	AB	a	2	0.000042	0.000028	0.000014	0.000042	0.000070
	IB	a	12	0.000608	0.000252	0.000010	0.000111	0.002210
	R	a	20	0.000130	0.000044	0.000005	0.000039	0.000795

2.3.1.2 Variation in peat properties with depth

Overall, bulk density decreased with depth for all three treatments except for the deepest sampling depth in the afforested bogs and the deepest two sampling depths in the restored bogs (Figure 2-2). Moisture content generally increased with depth except for fluctuations in the restored and afforested bogs, flattening off at depths greater than 60 cm. Carbon content declined at the 40 cm sampling depth in the intact bogs and 60 and 80 cm depths for the afforested and the restored bogs, respectively. S_y was not significantly correlated with sampling depth, although there was a weak negative correlation between S_y and bulk density ($r_s = -0.116$, $p = 0.001$, $N = 965$). Including all sites, a decline in S_y for afforested bogs over $0 - 40$ cm depths was followed by a spike at 50 cm and a steady increase between 60 and 100 cm depths. A consistent drop in S_y at 40 cm depths was evident at the two afforested raised bog locations but not at the blanket bog locations. S_y in the restored bogs for all sites remained relatively constant from the surface until 40 cm depth when there was a general increase in S_y towards 100 cm depth. However, a general increase in S_y with depth was observed in the raised bogs and a general decline in the blanket bogs. There was a sharp decline in S_y between 10 and 20 cm depth in the intact bogs, and then it remained relatively constant until 100 cm depth. Humification had the strongest positive correlation with depth ($r_s = 0.671$, $p < 0.001$, $N = 966$) whereas K_s had the strongest negative correlation ($r_s = -0.795$, $p < 0.001$, $N = 184$) with depth.
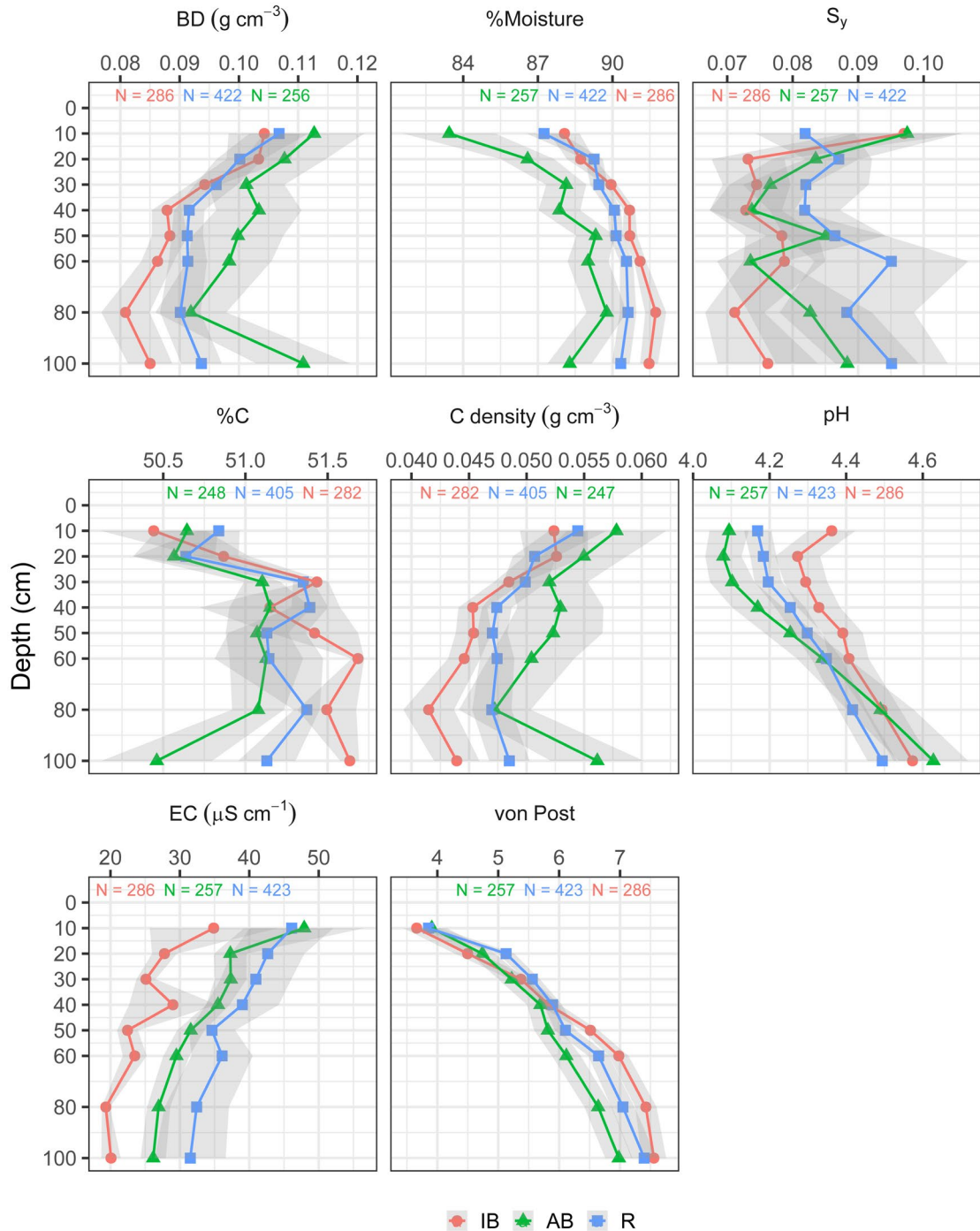
Figure 2-2 – Peat property means for the three main treatments (IB = intact bog, AB = afforested bog and R = forest-to-bog restoration) by depth (cm) ± standard errors. BD = bulk density; EC = electrical conductivity. The sample size for each treatment is given for each variable.

2.3.2 Differences between bog types and locations

There were significant differences in peat properties between the two different bog types (Table 2-3). Mann-Whitney tests showed that the blanket bog sites had higher

bulk density ($p = 0.13$, r = 0.09), lower moisture content ($p = 0.027$, r = 0.02), lower S_y ($p < 0.001$, r = 0.01) and more highly decomposed peat ($p < 0.001$, r = 0.21) than raised bogs, although effects were small. The pH was significantly lower ($p < 0.001$, Mann-Whitney, r = 0.73), and the electrical conductivity higher ($p = 0.006$, Mann-Whitney, r = 0.36) in the raised bog locations, with large and medium effect sizes, respectively.

Table 2-3 – Descriptive statistics for the two bog classifications for all treatments and depths up to 1 m. CLD = compact letter display (the same letters signify no significant difference between the bog types at the 95% confidence interval); N = sample size; SE = standard error of the mean; von Post estimates are given as 1 – 10 for the degree of humification. BD = bulk density; EC = electrical conductivity.

Variable	Class	CLD	N	Mean	SE	Min	Median	Max
BD (g cm^{-3})	BB	a	477	0.0979	0.0014	0.0100	0.0942	0.2500
	RB	b	487	0.0945	0.0014	0.0091	0.0900	0.2729
Moisture (%)	BB	a	478	89.35	0.20	32.89	90.03	98.56
	RB	b	487	89.37	0.18	64.14	90.06	98.55
C (% of dry mass)	BB	a	467	51.260	0.054	37.928	51.497	52.407
	RB	a	468	50.951	0.072	35.894	51.334	52.411
S_y	BB	a	478	0.0755	0.0020	0.0048	0.0688	0.3718
	RB	b	487	0.0907	0.0026	0.0033	0.0819	0.6093
von Post	BB	a	478	6.2	0.0813	1.1	6.3	9.5
	RB	b	488	5.5	0.0631	1.1	5.3	9.4
pH	BB	a	478	4.38	0.0144	3.54	4.40	5.15
	RB	b	488	4.25	0.0163	3.38	4.21	5.64
EC (µS cm^{-1})	BB	a	478	28.29	0.93	11	24	280
	RB	b	488	38.05	1.65	11	31	350
Infiltrometer K_s (cm s^{-1})	BB	a	12	0.001580	0.000226	0.000008	0.001542	0.002674
	RB	a	9	0.001151	0.000366	0.000001	0.000475	0.002634
Piezometer K_s (cm s^{-1})	BB	a	14	0.000355	0.000156	0.000005	0.000113	0.002210
	RB	a	20	0.000250	0.000131	0.000007	0.000039	0.002014

Averaged out for all treatments, there were no significant differences in K_s between the four locations. However, S_y was significantly different between all locations ($p < 0.05$, Kruskal-Wallis, $r > 0.008$). Flanders Moss had the highest S_y, and Talaheel had the lowest. Figure 2-3 gives the depth profiles for the measured variables for the intact sites from each of the four locations. Differences between the intact site locations showed greater overall effects for some variables than the land-use treatments (compare Figure 2-2 and 2-3). The largest effects were observed for bulk density ($p < 0.001$, Kruskal-Wallis, r = 0.686) and moisture content ($p < 0.001$, Kruskal-Wallis, r = 0.716) between the two blanket bog locations, and pH ($p < 0.001$, one-way ANOVA, $\eta^2 = 0.327$) between all locations.
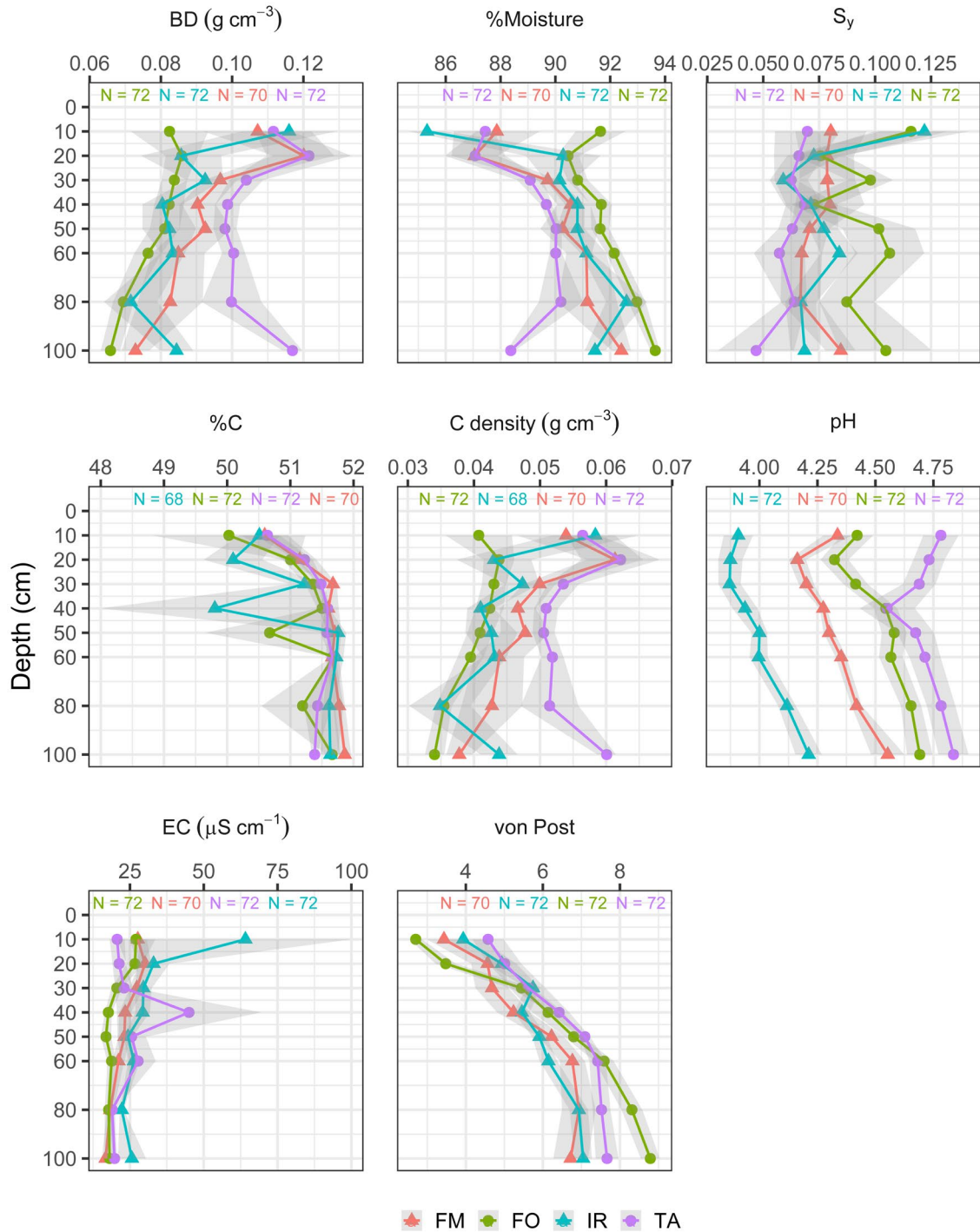
Figure 2-3 – Peat property means throughout the depth profile at the intact sites ± standard errors where FM = Flanders Moss; FO = Forsinain; IR = Ironhirst; TA = Talaheel. Triangles represent the raised bog points and circles the blanket bog points. BD = bulk density; EC = electrical conductivity. The sample size for each location is given for each variable.

2.3.3 Microtopographic differences

There were no significant differences in the peat properties measured between the intact bog microforms. The depth profiles are given in Figure A1-2. In the afforested

bogs (Figure A1-3), the peat in the furrows was significantly ($p < 0.001$, Kruskal-Wallis, $r > 0.32$) more humified than in ridges or the original surface. No significant difference was found in humification between the ridges and the original surface. In the restoration sites (Figure A1-4), the pH, moisture content, S_y, and humification were significantly higher in the furrows than ridges ($p < 0.01$, Kruskal-Wallis, $r > 0.15$), and the bulk density significantly lower ($p < 0.005$, Kruskal-Wallis, $r = 0.17$), although the effects were small.

2.3.4 Relationships between variables

Bulk density was negatively correlated with moisture content ($r_s = -0.855$, $p < 0.001$, $N = 965$) and with carbon content ($r_s = -0.258$, $p < 0.001$, $N = 935$). K_s was negatively correlated with humification ($r_s = -0.331$, $p < 0.001$, $N = 184$), pH ($r_s = -0.310$, $p < 0.001$, $N = 184$) and positively correlated with electrical conductivity ($r_s = 0.233$; $p < 0.005$, $N = 184$) and bulk density ($r_s = 0.196$; $p < 0.01$, $N = 184$). Conversely, humification was positively correlated with pH ($r_s = 0.384$, $p < 0.001$, $N = 966$) and negatively with electrical conductivity ($r_s = -0.335$, $p < 0.001$, $N = 966$). S_y was most strongly correlated with bulk density ($r_s = -0.116$, $p < 0.001$; $N = 965$) and electrical conductivity ($r_s = 0.137$, $p < 0.001$; $N = 965$), but it was the only measured variable not to have a significant correlation with K_s. Humification on the von Post scale was significantly correlated with all measured variables at the 95% confidence interval.

2.4 Discussion and Conclusions

2.4.1 Differences between treatments

The afforested bogs had significantly greater bulk density than other treatments, but there was no significant difference in bulk density between restored and intact bogs, and the effect size was small. Surprisingly, the degree of decomposition was only higher in the top 10 cm in the afforested bogs compared to the other treatments and not by a significant margin. Intact bogs had significantly lower electrical conductivity and greater pH than other treatments, but these variables were not significantly different between restored and afforested sites. Moisture content and carbon content were significantly different between the three treatments, highest in the intact and lowest in

the afforested bogs, while S_y and K_s did not differ between treatments. Again, most effect sizes were small except for a moderate difference between the afforested and intact bogs for carbon content and electrical conductivity between afforested/intact and restored/intact sites. Our spatial comparison suggests similar patterns to the time-series study by Anderson and Peace (2017), who observed decreased bulk density and increased moisture content of blanket bog 10 years following clear-felling and furrow blocking. Recovery was attributed to renewed buoyancy after re-wetting previously unsaturated near-surface peat and overburden pressure release from clear-felling (Anderson and Peace, 2017). However, we observed the highest variability for bulk density and moisture content in the afforested bogs. Mean bulk density ranged from 0.084 g cm^{-3} to 0.138 g cm^{-3} and moisture content from 83.0% to 90.4% and appeared independent of plantation age. However, given the variability and range of errors, it could be argued that there were no meaningful differences between treatments for bulk density, moisture and carbon content.

The lower carbon content in the afforested bogs suggests oxidative losses of CO_2 from the peat due to increased decomposition rates in aerobic peat through deeper water tables. The water table in the afforested site at Flanders Moss dropped to below 60 cm and at the afforested site at Forsinain water table was below 50 cm in the summer drought of 2018 (Howson *et al.*, 2021a), but it may have been lower outside our study period which would explain the lower carbon content throughout the depth profile. Higher electrical conductivities at the afforested and restoration sites could be due to legacy effects of acid interception and sea-salt scavenging (where sites were near the coast) from forest canopies, felled tree debris and litter inputs. However, the pH was variable between afforested sites; therefore, tree litter and felled waste may be the most likely source of solutes in afforested and restored bogs. Electrical conductivity was significantly higher in the afforested bogs at the blanket bog locations, but significantly higher values were observed in the raised bog restoration sites at Flanders Moss.

2.4.2 Differences between bog types and locations

There was no significant difference in bulk density, moisture content, carbon content, S_y, or K_s between intact raised and blanket bogs. The pH and degree of humification were significantly lower and electrical conductivity higher in the raised bogs than the blanket bogs with large, small and moderate effect sizes, respectively. The correlation between pH and humification may suggest decomposition, pH and water table-depth are interconnected. Less humified peats usually indicate shallower water tables; however, the substratum's pH can influence the degree of decomposition (Drzymulska, 2016). Studies have suggested lower pH can inhibit microbes associated with decomposition (Bridgham & Richardson, 1992; Ivarson, 1977), but the process may differ between anaerobic and aerobic peats (Bridgham & Richardson, 1992; Preston *et al.*, 2012). Therefore, the higher pH at the intact and restored blanket peatland sites may have influenced decomposition.

2.4.3 Microforms

No significant differences were found for the measured peat properties between the intact bog microforms. However, the degree of humification and S_y differed significantly between afforested microforms in the top 60 cm of afforested blanket peat. The only significant differences between microforms in the afforested raised bogs were the carbon content in the top 10 cm. Bulk density, moisture content, humification, S_y and pH differed significantly throughout the depth profile between microforms in the raised bog restoration sites, whereas only humification, moisture and carbon content differed significantly in the blanket bog restoration sites. Significant differences in compressibility, bulk density and K_s have previously been observed between intact microforms at specific depths, but high overall variability is typically reported (Baird *et al.*, 2016; Branham & Strack, 2014; Waddington *et al.*, 2010). Baird *et al.* (2016) found K_s, bulk density and humification highly variable between microforms, although it was suggested ridges were more highly decomposed with higher bulk densities than hollows. However, our study suggests that any differences between intact microforms in the top metre of peat were insignificant compared to changes brought about by forest ploughing and restoration.

Forest ploughing likely explains the differences in humification profiles between afforested microforms where the top 30 - 50 cm of peat in the furrows is removed, and the resulting ridges would be a mixture of the top layers from the furrows. The top layers in furrows immediately after ploughing would be equivalent to 30 - 50 cm below the original surface. In the restored bogs, the humification below ridges and the original surface was closer to that below furrows than in the afforested bogs. Since planting, furrows can infill with mosses and tree litter, potentially explaining the convergence in humification profiles. As might be expected, the moisture content below furrows was higher, particularly at shallow depths, in the restored bogs than in the afforested bogs. However, differences in pH between the furrows and the other microforms in the restored bogs were greater than in the afforested bogs.

2.4.4 Implications for hydrology

The flow of water and solute transport in peatlands are closely linked with peat physical properties. In this study, K_s ranged from 2.67 x 10^{-3} cm s^{-1} to 5.53 x 10^{-7} cm s^{-1}, similar to those reported in other peatland studies (Baird *et al.*, 2016; Lewis *et al.*, 2012), with no significant difference observed between treatments. Therefore, despite the difference in bulk density, subsurface flow through the upper layers of peat may not differ significantly between treatments. These similarities in K_s may explain the streamflow at the sites at Forsinain measured by Howson *et al.* (2021b), where flow duration curves were comparable between intact, afforested and restored sites. Surface infiltration rates between the Flanders Moss and Forsinain afforested sites were not significantly different, suggesting other factors such as tree age influenced the difference in water-table dynamics reported by Howson *et al.* (2021b).

2.4.5 Conclusion

Overall, the hypothesis that peat properties in the afforested bogs would be significantly different to those in the intact bogs, while peat properties for restored bogs would lie somewhere in between is largely accepted. However, the minimum effect size (η^2 and r) for differences in pH, electrical conductivity, K_s and S_y between the different intact bogs were 0.295 (η^2), 0.009 (r), 0.077 (r) and 0.007 (r) greater than

those between land-use treatments, respectively. Therefore, natural variability between locations and peatland type must be considered when interpreting land management impacts on peatland properties and functioning.

2.5 Acknowledgements

2.6 References

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Chapter 3: A comparison of porewater chemistry between intact, afforested and restored raised and blanket bogs

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Abstract

Afforestation is a significant cause of global peatland degradation. In some regions, afforested bogs are now undergoing clear-felling and restoration, often known as forest-to-bog restoration. We studied differences in water-table depth (WTD) and porewater chemistry between intact, afforested, and restored bogs at a raised bog and blanket bog location. Solute concentrations and principal component analysis suggested that water-table drawdown and higher electrical conductivity (EC) and ammonium (NH_4-N) concentrations were associated with afforestation. In contrast, higher dissolved organic carbon (DOC) and phosphate (PO_4-P) concentrations were associated with deforestation. Drying-re-wetting cycles influenced seasonal variability in solute concentrations, particularly in shallower porewater at the raised bog location. WTD was significantly deeper in the oldest raised bog restoration site (~9 years post-restoration) than the intact bog (mean difference = 6.2 cm). However, WTD in the oldest blanket bog restoration site (~17 years post-restoration), where furrows had been blocked, was comparable to the intact bog (mean difference = 1.2 cm). When averaged for all porewater depths, NH_4-N concentrations were significantly higher in the afforested than in the intact sites (mean difference = 0.77 mg L^{-1}). In contrast, significant differences between the oldest restoration sites and the intact sites included higher PO_4-P (mean difference = 70 µg L^{-1}) in the raised bog and higher DOC (mean difference = 5.6 mg L^{-1}), EC (mean difference = 19 µS cm^{-1}) and lower $SUVA_{254}$ (mean difference = 0.13 L mg^{-1} m^{-1}) in the blanket bog. Results indicate felled waste

(brash) may be a significant source of soluble C and PO_4-P. Mean porewater PO_4-P concentrations were between two and five times higher in furrows and drains in which brash had accumulated compared to other locations in the same sites where brash had not accumulated. Creating and maintaining brash-free buffer zones may therefore minimise freshwater impacts

3.1 Introduction

Peatlands are highly important ecosystems, responsible for a third of the global soil carbon pool (Scharlemann *et al.*, 2014; Yu *et al.*, 2010) and essential for a range of other ecosystem services (Bonn *et al.*, 2016), despite covering less than 3% of the Earth's land area (Xu *et al.*, 2018). Historically, the condition of peatlands has been influenced by land management, with an estimated 15% of peatlands globally now in a non-natural state (Joosten, 2016). Large-scale deforestation of naturally forested peatlands or afforestation of treeless peatlands with non-native trees for timber (Päivänen & Hånell, 2012) or palm oil production (Joosten, 2016) are significant sources of peatland degradation (Menberu *et al.*, 2016; Ramchunder *et al.*, 2012). More than half of Finland's formerly accumulating peatlands have been forestry-drained, mainly between 1960 and 1990 (Strack, 2008) and in the UK, non-native coniferous trees have been planted on previously open peatlands since the 1940s with up to ~190,000 ha of deep peat afforested between 1950 and the 1980s (Cannell *et al.*, 1993; Hargreaves *et al.*, 2003).

Recognition of the biodiversity value and the carbon sequestration (Apps *et al.*, 1993; Simola *et al.*, 2012) potential of peatlands has led to increased efforts to protect and restore these ecosystems in the UK (Andersen *et al.*, 2017; Parry *et al.*, 2014) and globally (Rochefort & Andersen, 2017). Attempts to restore previously afforested fen and bog peatlands have occurred in many parts of Europe and some areas of North America (Andersen *et al.*, 2017; Anderson *et al.*, 2016; Chimner *et al.*, 2016). Earlier restoration in Scandinavia (Haapalehto *et al.*, 2011; Komulainen *et al.*, 1999) predates much of the work carried out in the UK, but forest-to-bog restoration is still a relatively new practice. Therefore, there has been limited opportunity to study the long-term

effects of large-scale deforestation on water-table depth (WTD) and water quality to support peatland restoration. Also, it is not clear if different peatland types respond similarly or not to forest-to-bog restoration.

Conifer plantations on peatlands lower the water table through drainage and evapotranspiration (Anderson, 2001). Restoration (Figure 3-1) requires forest clearance to raise the water table, which is a critical factor for the hydrological functioning of bogs (Anderson, 2001; Holden *et al.*, 2004; Price *et al.*, 2016). Forest clearance alone may not result in sufficient change in water-table levels to bring about restoration in the short term (Anderson & Peace, 2017). Therefore, drainage ditches and furrows may be blocked to assist in the recovery of the water table (Anderson & Peace, 2017; Haapalehto *et al.*, 2014; Haapalehto *et al.*, 2011). However, few UK studies report peatland restoration after conifer felling results in water-table levels that are similar to those in undisturbed peatlands.

There are a range of forest clearance methods that can result in different amounts of forest biomass being left on the site, which potentially affects water quality. At some restoration sites, usually, those where the forest is being felled early for peatland restoration, the trees are left to decompose naturally on the ground or have even been compressed into furrows and drains to slow the flow of water (Muller *et al.*, 2015). At others, most of the timber and felling debris (i.e. branches and tops) has been removed using low impact techniques (Shah & Nisbet, 2019). Residues from decaying forest debris can be an important source of nutrients and organic matter (Gaffney, 2017; Gaffney *et al.*, 2018; Muller *et al.*, 2015; Muller & Tankéré-Muller, 2012; Shah & Nisbet, 2019) entering adjacent watercourses with the potential to affect sensitive aquatic species such as Atlantic salmon, *Salmo salar*, and freshwater pearl mussel, *Margaritifera margaritifera*, both legally protected species (Shah & Nisbet, 2019). Mulching of whole trees is an alternative to conventional harvesting and is sometimes used where the trees have little or no commercial value and where extraction could cause further damage to soil and water. However, little is known about the effects of mulching on water quality.
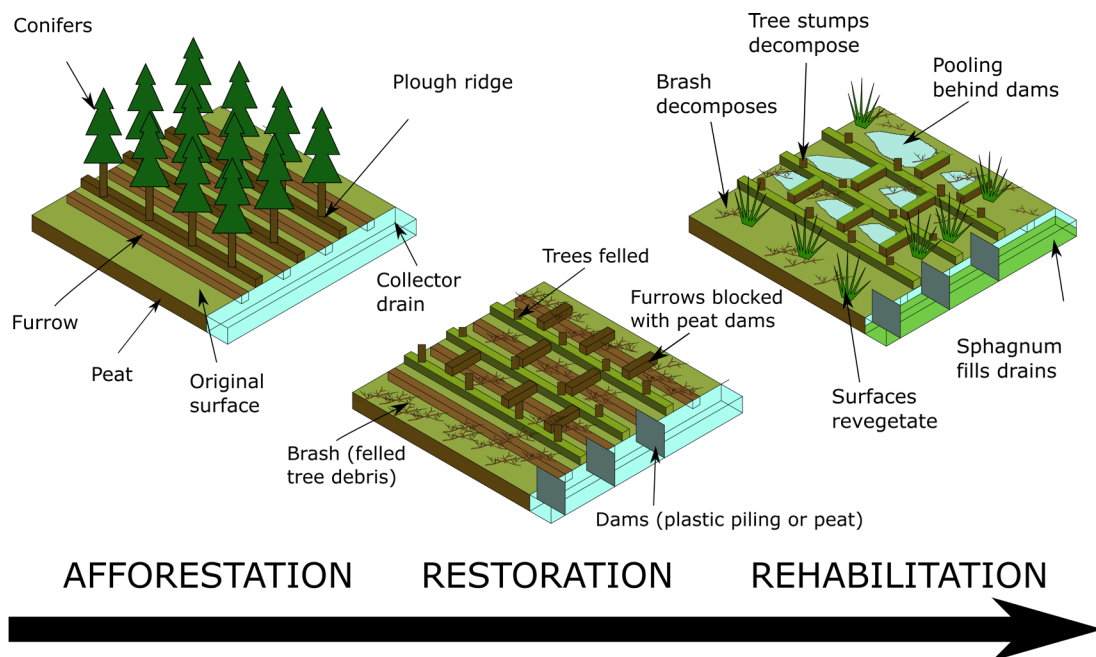
Figure 3-1 – Typical forest-to-bog restoration process - i) afforestation of peatland for commercial gain and forest matures (30-50 years); ii) forest is felled; ideally, timber is harvested, drains, and furrows are typically blocked to raise water-table levels; iii) peatland is left to rehabilitate to restore pre-afforestation ecosystem function.

Most forest-to-bog restoration studies in the UK have occurred on blanket bogs, and those that have examined water quality have focussed mainly on streamwater (Table 3-1). As bogs are ombrotrophic (i.e. receive nutrients mainly via precipitation), internal nutrient cycling is essential, and changes in nutrient cycling are tightly coupled to the carbon cycle (Gaffney *et al.*, 2018; Keller *et al.*, 2006; Oviedo-Vargas *et al.*, 2013). In the UK, only Gaffney *et al.* (2018) has looked at differences in porewater quality between forested, intact and restored sites finding the lasting legacies from afforestation were elevated NH_4-N and acidity 17 years after felling as well as incomplete WTD recovery. The influence of forestry on soil water pH is well established, although it has become less of an issue in recent times (Drinan *et al.*, 2013; Fowler *et al.*, 1989; Harriman & Morrison, 1982; Nisbet & Evans, 2014; Nisbet *et al.*, 1995). However, the conclusions of Gaffney *et al.* (2018) were based on a limited programme of sampling on three occasions during the growing season and only on a blanket peatland. Thus, there is a need to expand the range of peat types and the frequency and duration of study post-felling to get a better understanding of the processes controlling porewater chemistry at different times.

Table 3-1 – Peatland conifer plantation restoration studies examining water quality. MF = minerotrophic fen; PF = nutrient poor fen / bog; BB = Blanket bog; RB = Raised bog; SS = soil samples; SW = streamwater; PW = porewater; TF = trees felled; TM = trees mulched; DD = drains dammed; DI =drains infilled; CF = brash compacted in furrows; LIH = low-impact harvesting; WTD = water-table depth.

Study	Location	Peatland type	Sample type	Restoration techniques	Time since felling	Key findings
Haapalehto *et al.* (2011)	Finland	MF/RB	SS	TF/DD/DI	0-10 years (if growth sufficient)	Elemental concentrations of Ca, K, Mg, Mn, and P were comparable to pristine peatlands 10 years after restoration.
Koskinen *et al.* (2011)	Finland	MF/PF	SW	TF/DD/DI	0-6 years (PF only)	MF leached more N, less dissolved organic carbon (DOC) and P than PF.
Sallantaus and Koskinen (2012)	Finland	MF/PF	SW	TF/DD/DI	0-7 years (PF only)	P elevated for 6 years in the PF. 6 times higher after 6 years in MF.
Muller and Tankéré-Muller (2012)	Scotland	BB	SW	TF/CF	0.5-1.5 years	Al and Mn influenced by felling. Forest buffer strips counteract mobilisation of DOC, K, and Fe.
Haapalehto *et al.* (2014)	Finland	MF/RB	PW	TF/DD/DI	0-10 years (if growth sufficient)	Long-term decrease in DOC and nutrient leaching were observed, but temporary increases in N and P for the first 5 years.
Muller *et al.* (2015)	Scotland	BB	SW	TF/TM/CF	~2 years	Spikes in DOC, Al, Fe, K, Mn, P year following felling. DOC-4, K-6, and P-15 times higher than near-natural bog after two years.
Koskinen *et al.* (2017)	Finland	MF/PF	SW	TF/DD/DI	0-4 years	Elevated DOC, N, and P 4 years after restoration. Less of an issue in PF.
Gaffney *et al.* (2018)	Scotland	BB	PW/SW	TF/TM/DD/CF	0-17 years.	WTD, pH and NH_4^+ in PW main barriers to restoration success.
Shah and Nisbet (2019)	Scotland	RB	SW	TF/LIH	0–9 years	Elevated phosphate returned to pre-felling levels after 3-5 years. DOC elevated 4 years after restoration. pH impacts varied with a significant increase at one site.

Although conifer afforestation on peat can increase dissolved organic carbon (DOC) concentrations in porewater (Grieve & Marsden, 2001) through increased mineralisation as a result of lower water tables and increased litter production, the most significant increases in streamwater concentrations of DOC have been reported after felling (Evans *et al.*, 2005). Several studies where clear-felling and drain-blocking have taken place documented increases in DOC and nutrients (Koskinen *et al.*, 2011; Koskinen *et al.*, 2017; Muller *et al.*, 2015; Muller & Tankéré-Muller, 2012; Sallantaus & Koskinen, 2012) as have studies limited to clear-felling and forest harvesting (Asam *et al.*, 2014b; Clarke *et al.*, 2015; Nieminen *et al.*, 2015; Palviainen *et al.*, 2014; Rodgers *et al.*, 2010; Shah & Nisbet, 2019). However, time frames for recovery to pre-

felling levels vary from 3-5 years (Shah & Nisbet, 2019) to greater than 10 years (Palviainen *et al.*, 2014) for N and P. Shah and Nisbet (2019) recommended that less intensive harvesting techniques can help reduce these negative impacts. However, more information is required to understand the transport mechanisms of DOC and nutrients from the point of source to watercourses.

Given the lack of studies that have compared the impact of forest-to-bog restoration on porewater quality and WTD at different peatland types over time, the objectives in this study were to:

i. Determine whether significant differences in WTD and porewater chemistry exist between intact, afforested, and restored bog sites.

ii. Investigate whether differences exist in the response of porewater chemistry to forest-to-bog restoration at different depths in the peat (20 to 80 cm)

iii. Quantify seasonal variability in WTD and porewater chemistry in intact, afforested, and restored bog sites and determine whether significant differences exist.

iv. Compare and contrast the impact of forest-to-bog restoration on porewater DOC and nutrients at a raised bog and blanket bog peatland.

3.2 Methods

3.2.1 Study sites

The blanket bog (BB) sites in this study are located at Forsinain in the 'Flow Country' area of northern Scotland (Figure 3-2), the largest blanket peatland in Europe (c. 4000 km^2). The land was previously owned by the Forestry Commission and has subsequently been acquired by the Royal Society for the Protection of Birds (RSPB) as part of the Forsinard Flows National Nature Reserve (NNR) in Sutherland (58° 24'43.2 "N, 3° 52'25.0 "W). The raised bog (RB) sites are located at Flanders Moss, part of a group of lowland raised bogs formed on the Carse of Stirling in Central Scotland (56°

08'10.5 "N, 4° 19'28.7 "W) and are managed by Forestry and Land Scotland (previously Forestry Commission Scotland) and Scottish Natural Heritage. The annual mean rainfall between 1981-2010 (Met Office *et al.*, 2018) was 1444 mm at Flanders Moss and 1097 mm at Forsinain. The annual mean temperature was 8.7 °C at Flanders Moss and 7.4 °C at Forsinain over the same period.

Standing forestry plantation sites (hereafter referred to as afforested bog (AB)) and open, near-natural bog (hereafter referred to as intact bog (IB)) were included to represent the different land-management types. Two restored (R) sites of different ages since restoration (R1 > R2), and using slightly different restoration techniques, were selected at both locations (Table 3-2). All sites were broadly comparable at each location in terms of slope, and the afforested sites were carefully chosen so that the whole area was under canopy cover.

Table 3-2 – Site characteristics at Flanders Moss (RB) and Forsinain (BB) where CA = catchment area (ha); Nest labels = unique sampling location IDs (referred to later). Felled-to-waste = trees felled, but timber and brash not extracted.

Site	Description	CA (ha)	Nest labels	Tree clearance dates	Restoration method	Furrow spacing	Planting year
RBIB	Intact raised bog	6.0	24,26,28,32				
RBAB	Afforested raised bog	0.2	72,73,74,75			1.4 m	~1965
RBR1	Restored raised bog	2.5	10,11,12,13	24/11/2009-09/12/2009 01/08/2011-18/10/2011	Part conventional harvesting; part low impact harvesting and removal of brash and logs.	1.4 m	~1965
RBR2	Restored raised bog	26.2	16,17,21,22	01/10/2013-31/03/2014	Conventional harvesting (i.e. fell, debranch, extract timber, leave brash).	1.4 m	~1965
BBIB	Intact blanket bog	1.6	45,46,47,48				
BBAB	Afforested blanket bog	5.1	63,64,65,66			1.9 m	~1980
BBR1	Restored blanket bog	1.6	33,34,35,36	2002-2003	Felled-to-waste/furrows & main drain blocked.	1.4 m	~1980
BBR2	Restored blanket bog	2.3	37,38,39,40	2014-2015	Mulched/main drain blocked.	2.3 m	~1980
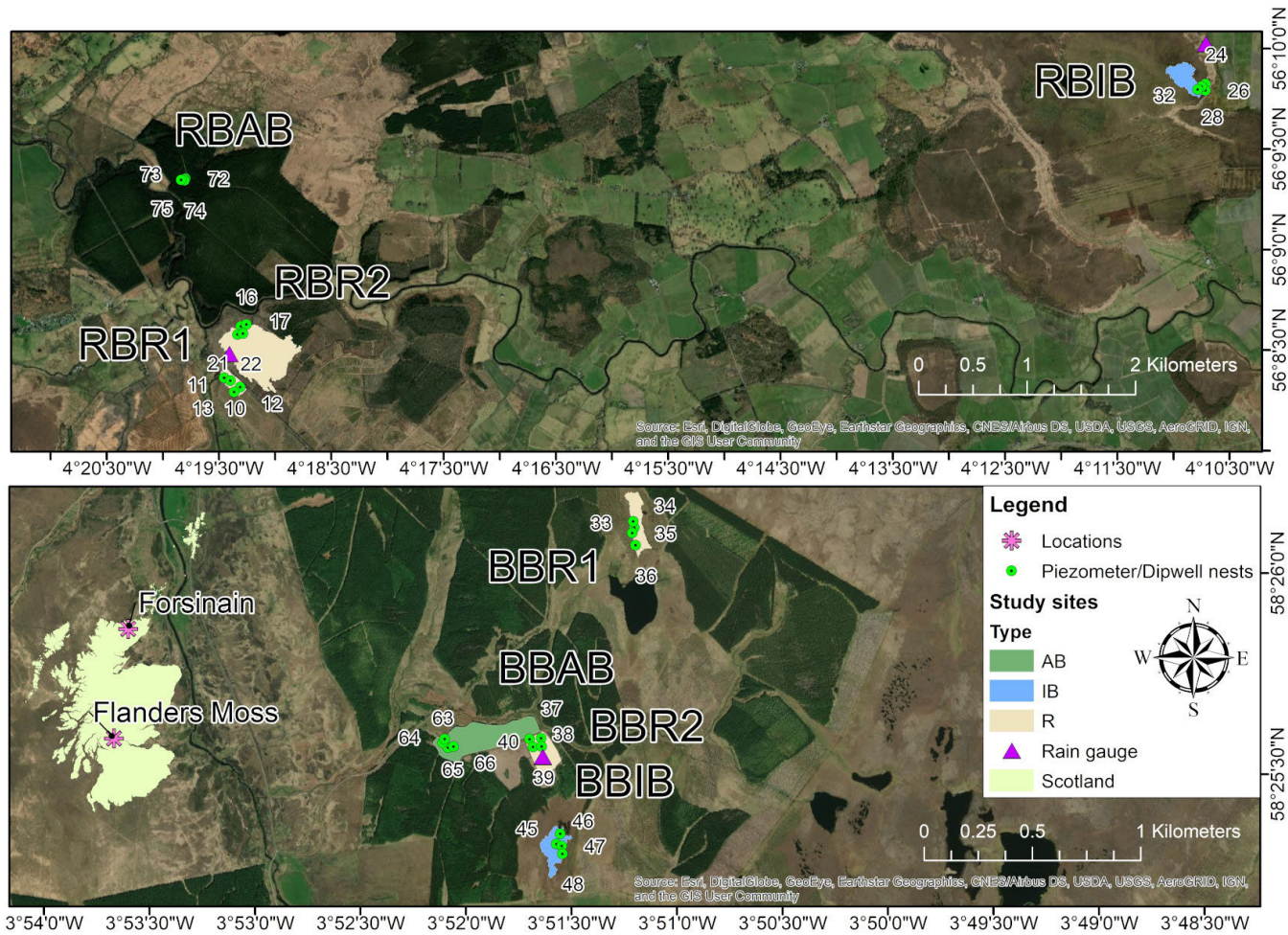
Figure 3-2 – Study site experimental design at Forsinain (BB) and Flanders Moss (RB); AB = afforested bog; IB = intact bog; R1 =oldest restoration site; R2 = most recent restoration site. The numbers represent instrument nest labels.

RBIB represented the best example of intact bog in the area with a mosaic of sphagnum mosses (including some nationally scarce species: *S. austinii*, *S. fuscum* and *S. molle*), sedges, ericaceous shrubs, and sundews (*Drosera spp.*). RBAB, RBR2 and RBR1 were drained in the 1920s to improve conditions for grouse shooting, and in the 1960s and 1970s were ploughed and planted with lodgepole pine (*Pinus contorta*) and Sitka spruce (*Picea sitchensis*). Records of fertiliser application at the time of planting are not available, but an application of NPK fertiliser was customary in afforestation schemes of that period (Shah & Nisbet, 2019). The first rotation forest at RBR2 was harvested over 6 months between 2013-14 using a conventional harvester and forwarder (Shah & Nisbet, 2019). The tree stems were extracted, but much of the brash, comprising branches and tops, was left on site to decompose. RBR1 was felled in two phases: the first in the winter of 2009 (15%) and the remainder in summer/autumn 2011. The first phase of felling was carried out using standard forest harvester and forwarder techniques with forest materials, including brash, left *in situ*. The second phase was carried out by hand felling and winching the main stems out using an overhead Skyline (Shah & Nisbet, 2019), after which all useable timber and brash were removed and chipped for biomass. Neither drain nor furrow blocking had taken place at the raised bog restoration sites at the time of the study.

The vegetation at BBIB is similar in composition to that at RBIB with the addition of liverworts, bog asphodel (*Narthecium ossifragum*) and bogbean (*Menyanthes trifoliata*) in pools. At the southern end of BBIB, there was evidence peat cutting had once taken place and forestry had been planted to the east and west, but mainly it is a good example of near-natural bog, typical to the area, with natural pool complexes in the north. In the 1980s, the blanket bog was drained and planted with the same mixture of tree species as the raised bog, but there was a difference in the ploughing/planting phase, with the furrows being 50 and 90 cm further apart in BBAB and BBR2, respectively. However, the furrows were similarly spaced to those at the raised bog in BBR1 (Table 3-2). It is likely but cannot be assumed that a standard application of NPK fertiliser would have been used at the time of planting.

BBR2 differed from the other restoration sites in that it was the only site where the trees had been 'whole-tree mulched' in 2014, most likely using a mechanical masticator mounted on the arm of an excavator (Moffat *et al.*, 2006; Muller *et al.*, 2015). Whole-tree mulching is an alternative to conventional felling where the trees are essentially chipped from standing, often used when the forest is being felled early, growth has been so weak that harvesting would entail a net cost, there are access constraints and the potential for site damage resulting in environmental impacts. It has the practical advantages of not requiring timber extraction, leaving less coarse debris on the surface of the peat and can potentially reduce soil and water damage as there is reduced machine trafficking. The main drain at BBR2 was also blocked with a sequence of three plastic piling dams close to the outflow, and additional peat dams were added at regularly spaced intervals on 23rd March 2019. BBR1 was felled in 2002/3 when the trees were still young (~20 years old), but any felled material was not extracted (felled-to-waste). Instead, it was compressed into the furrows, which were later blocked with peat dams in 2015/16, the same time as the main drain.

3.2.2 Field sampling and measurements

Within each site, four nests, consisting of four piezometers at 20, 40, 60 and 80 cm depths to collect soil water, and a dipwell for monitoring WTD (Figure 3-2), were carefully inserted into the peat after a hole had been augured of a slightly smaller diameter than the tubes. The piezometers were constructed from 19.05 mm internal diameter PVC tubing, cut to length, with 0.5 cm holes drilled in a ring at the sampling depth, and two further rings of holes drilled ±1 cm on either side. Therefore, the porewater was sampled over a ~2.5 cm range at each depth. There was a 5 cm reservoir at the bottom of the piezometer to collect water. Air holes were drilled well above the surface to allow venting but prevent the ingress of overland flow, and a flush-fitting plug formed a watertight seal at the base. The dipwells were constructed from similar PVC tubing, generally > 1 m in length and with 0.5 cm holes drilled at 3.5 cm intervals throughout the length of the tube with four holes at each interval. The base was sealed with a PVC plug. Caps were fitted to the tops of both piezometers and dipwells to prevent debris and insect ingress.

The piezometer-dipwell nests were allocated random locations within each site, using the "Create Random Points" tool in ArcGIS (ESRI, 2017), generally > 30 m apart, and stored as waypoints in a handheld GPS. Each piezometer was labelled with a unique nest number followed by a letter A – D representing the sampling depth (where A = 20, B = 40, C = 60, D = 80 cm). The nest locations represented a range of surface features associated with afforestation and natural bog microforms (restored and afforested - ridges, furrows and original surface; intact - hollows, hummocks and lawns) and different mixtures of vegetation, which were recorded during the installation. A tipping bucket rain gauge was installed at the blanket bog, where the sites were relatively close to each other (BBR2: Davis 6465 + HOBO UA00364 event logger). Two tipping bucket rain gauges were installed at the raised bog (RBR1: Davis 7852 + HOBO H07-002-04 event logger; RBIB: Davis 6465 + HOBO UA00364 event logger) to account for any localised rainfall differences between the sites. The tipping buckets measured 0.2 mm of rainfall for every recorded logger event. Air temperature observations were taken from the 1 km HadUK-Grid (Met Office *et al.*, 2018). The closest weather stations with continuous air temperature records for the study period were Bishopton, Glasgow for Flanders Moss (27.3 km), and Kinbrace for Forsinain (17.5 km).

The piezometer-dipwell nests were installed at different times, but porewater samples and WTD measurements were not taken until at least a month had elapsed following installation. Before taking the first samples, any peat obscuring the piezometer intakes was removed by repeatedly emptying them with a plastic syringe and allowing them to refill until the extracted water was clear. When sampling the piezometers, the sampler knelt in large gravel trays to distribute their weight and avoid peat compaction from trampling. The porewater chemistry and WTD were monitored at each site from April 2018 until November 2019. Manual dipwell readings were taken on each site visit using a steel capillary tube with a self-adhesive scale. All piezometers were emptied of any water and sampled the following day into a 50 mL centrifuge tube using a plastic syringe connected to a 1 m PVC hose rinsed with deionised water between samples. During dry periods, there was not always a collectable sample at 20 and 40 cm, particularly in the afforested sites. All porewater samples were packed with ice packs in an insulated box for refrigerated transport back to the laboratory.

Porewater samples were collected monthly from April to August 2018 and then at two-monthly intervals thereafter until November 2019 ($n = 12$; 1164 samples), except for a gap during winter due to site inaccessibility (December 2018 – March 2019). Measurements of pH and electrical conductivity (EC) were made on return to the laboratory using a HANNA 9124 pH meter and HORIBA B-173 EC meter.

3.2.3 Chemical analysis

Samples were vacuum filtered through 0.45 µm cellulose acetate filters, usually within 48 hrs and then analysed for nutrients using colorimetry (Skalar San++ colorimetric auto-analyser) and dissolved organic carbon (DOC) by combustion (Analytik Jena Multi N/C 2100C combustion analyser). The following nutrients were determined using the auto-analyser: dissolved ammonium-nitrogen (NH_4-N), soluble reactive phosphate as phosphorus (PO_4-P), total oxidised nitrogen (TON) and nitrite-nitrogen (NO_2-N) with detection limits of 0.01, 0.005, 0.16 and 0.002 mg L^{-1}, respectively. Nitrate-nitrogen (NO_3-N) concentrations were determined by subtracting NO_2-N from TON. The methods for DOC and nutrients are covered in more detail in Appendix A2. Additionally, water colour was measured by absorbance at 254 nm, 465 nm and 665 nm using a spectrophotometer (Jasco V-630 double beam spectrophotometer). Absorbance readings were converted to standardised water colour measurements of absorbance units per metre (abs m^{-1}).

Humic and fulvic acids are the dominant components of DOC and absorb light at different wavelengths in different quantities. As a result, the ratio of absorption at 465 nm and 665 nm, known as the E4:E6 ratio, gives an indication of the proportion of humic and fulvic acids and hence the degree of humification as humic acids are more mature than fulvic acids (Grayson & Holden, 2011; Strack *et al.*, 2015). Thurman (1985) observed that humic acids from soils had an E4:E6 of 2 to 5, whereas fulvic acids had a ratio of 8 to 10. However, in some waters, little absorption occurs at 665 nm, so absorption at 254 nm, when normalised to the DOC concentration, has been used instead of E4:E6 as an indicator of aromaticity (Helms *et al.*, 2008; Weishaar *et al.*, 2003). The result, known as specific UV absorption ($SUVA_{254}$), was found by

Weishaar et al. (2003) to correlate strongly with DOC aromaticity, as determined by 13C-nuclear magnetic resonance (13C-NMR). Higher values indicated greater aromaticity and, therefore, greater hydrophobicity.

3.2.4 Data analysis

Solute boxplots were used as a visual comparison of the spread of the data using the ggplot2 package (Wickham, 2016) in R Studio (RStudio-Team, 2016) for shallow (20-40 cm) and deep (60-80 cm) sampling depths at each site. Although peat depths were generally greater than 1 m, four equal depth increments were chosen in the top 80 cm to account for water-table drawdown in the forestry and to ensure no mineral material below the peat was disturbed. Time-series data were produced by taking the month and year of the sampling date, and statistical summaries were used for plotting mean monthly values and standard errors.

Other statistical analyses were performed in SPSS (IBM Corp., 2016), by firstly testing for normality and homogeneity of variance, and where possible parametric ANOVA tests of differences in the mean values of each group were used to test any hypotheses and identify any interactions between sites, location (Flanders Moss/Forsinain) and sampling depth. Where the data deviated from a normal distribution or homogeneity of variance was not satisfied, it was transformed in SPSS, or non-parametric Kruskal-Wallis tests were used. *Post-hoc* tests were used to determine significant differences for parametric tests, and pairwise comparisons were used for the same purposes for non-parametric Kruskal-Wallis tests. Spearman's rank coefficients (r_s) were calculated in SPSS to assess any non-parametric correlations between variables. Mann-Whitney U tests were used for non-parametric analysis in testing for differences between the locations. Generalised Linear Mixed Models were used in SPSS to assess the independence of repeated measurements using 'Compound Symmetry' as the covariance type, the unique piezometer identifier as the subject and the sampling month as the repeated variable.

Principal component analysis (Jolliffe & Springer-Verlag, 2002) was carried out on the porewater variables at both locations using the three main treatments (intact, afforested, restored) as groups. Scree plots were produced to examine the variances of the principal components selecting all nutrient variables, DOC, WTD, air temperature, pH, and EC. Biplots, using the 'ggbiplot' package in R Studio (Vu, 2011), were generated to examine any clustering of observations with respect to the variable loadings and the first two principal components. The piezometer-dipwell nest label was used to identify individual observations to assess any outliers. The variable loadings gave a visual representation of their significance for the three different treatment groups and any relationships they may have. Any solute values below the detection limits of the instruments were substituted by the detection limit divided by the square root of two (Croghan & Egeghy, 2003). Outliers were preserved.

3.3 Results

3.3.1 Climate conditions during the study

The total monthly rainfall and mean monthly air temperatures from April 2018 until the end of November 2019 are shown in Figure 3-3 for both the raised bog and the blanket bog locations. Over the study period, the blanket bog was over a degree cooler, and there was 36 mm less precipitation than the raised bog. For 2018, the annual precipitation from the on-site rain gauges was 1001 mm at the raised bog and 742 mm at the blanket bog, which is considerably less than the mean annual figures of 1444 mm and 1097 mm at the raised bog and the blanket bog, respectively (Met Office *et al.*, 2018). Mean monthly temperatures during the study ranged from 3.4 to 16.6 °C at the raised bog and 2.4 to 15.4 °C at the blanket bog. Between April 2018 and August 2018 was unusually hot and dry at both locations, and at the blanket bog, no rain was recorded for 36 consecutive days between the 15th June and 21st July. 2018 was one of the hottest summers on record, with a longer-lasting drought at the blanket bog location. However, in the 2019 study year, the blanket bog rain gauge recorded 146 mm higher total precipitation than the RBIB rain gauge.
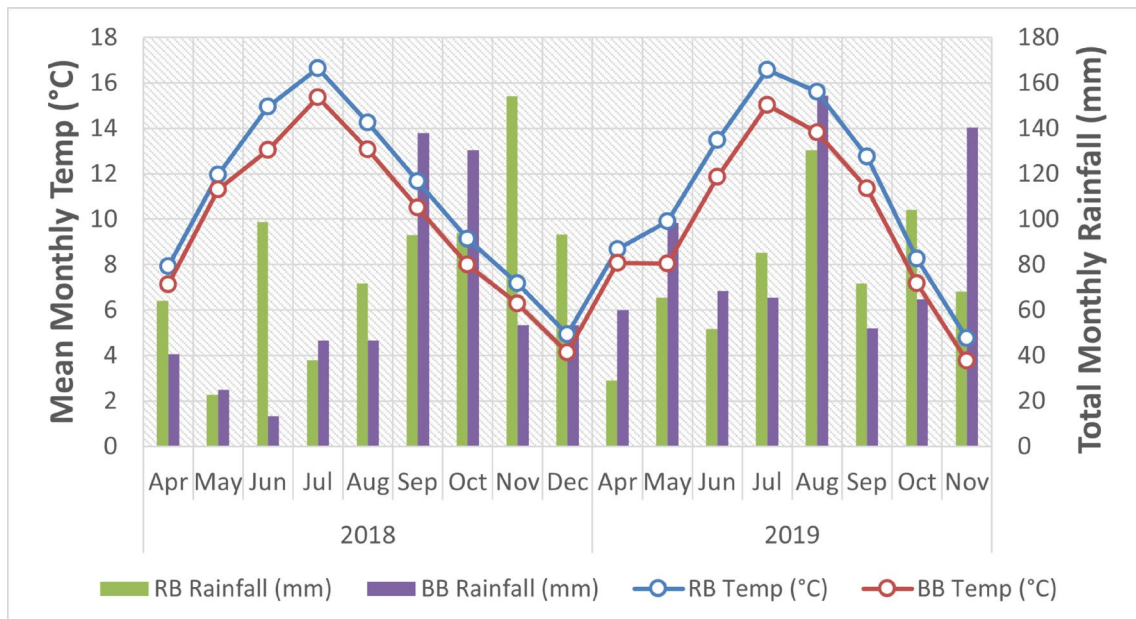
Figure 3-3 – Temperature and rainfall at Forsinain (BB) and Flanders Moss (RB) over the study period. Rainfall for the raised bog is taken from the RBIB rain gauge.

3.3.2 Water-table depth

Water-table drawdown in the forestry sites was evident at both raised and blanket bog locations (Figure 3-4). There was a significant difference ($p < 0.001$, one-way ANOVA) in WTD between the afforested (deepest) and the intact bog (shallowest) sites. The mean WTD at RBAB was 30.6 cm compared to 9.8 cm at RBIB. The average WTD was also significantly deeper ($p < 0.05$, one-way ANOVA) at RBR1 (16.0 cm) and RBR2 (20.7 cm) than RBIB. The mean WTD at BBAB was 25.6 cm compared to 9.6 cm at BBIB. However, the mean WTD for both BBR1 (8.4 cm) and BBR2 (11.9cm) were not significantly different ($p =0.855$, one-way ANOVA) to BBIB. Overall, the mean WTD was significantly deeper ($p = 0.002$, one-way ANOVA) at the raised bog (18.0 cm) than the blanket bog (13.8 cm) location, and there was a significant interaction ($p < 0.001$, two-way ANOVA) between the location and the sampling month which highlighted significant seasonal differences existed between the two locations (Figure 3-4).
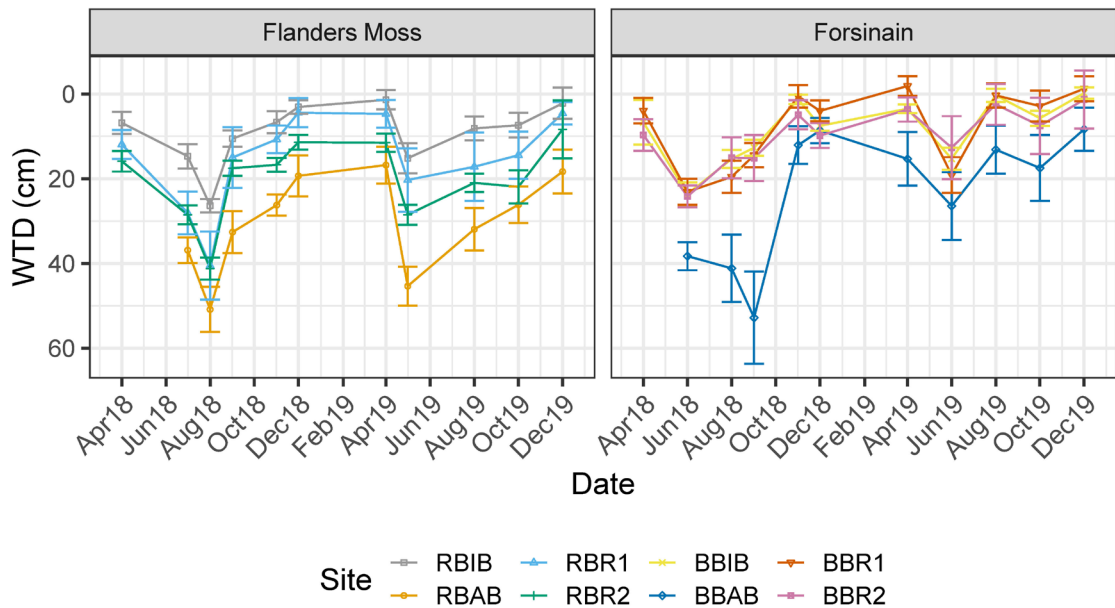
Figure 3-4 – Time series of water-table depth (WTD) ± SE for the sites at both locations. RB = raised bog; BB = blanket bog; IB = intact bog; AB = afforested bog; R1 = oldest restoration site; R2 = most recent restoration site.

WTD displayed a strong seasonal pattern at both locations (deeper in summer and shallower in winter), reflecting the rainfall and evapotranspiration patterns over the study period (Figure 3-4). On average, WTD was 0.2 cm deeper at RBIB than BBIB and 5.0 cm deeper at RBAB than BBAB, but the differences were not statistically significant. The difference in the WTD between the afforested site and the other sites was larger in the unusually dry period of spring/summer 2018 at the blanket bog and in May 2019 at the raised bog location. The water table at BBAB receded beyond that of RBAB in the 2018 summer drought but remained shallower during the following summer (Figure 3-4). In wetter periods, the differences in WTD between the treatments decreased, especially at the blanket bog location. There was a divergence between BBAB and the other blanket bog sites in July and August 2018, where rainfall was sufficient to raise the water table in the restored and intact sites but not in the afforested site.

3.3.3 Porewater chemistry

Boxplots of the main porewater variables for each study site are presented in Figure 3-5. A small proportion of NH_4-N, PO_4-P and NO_2-N (0.3%, 7.0% and 14.0%,

respectively) concentrations were below detection limits, whereas the majority (98.4%) of TON concentrations were below the detection limit. NH_4-N concentrations at RBAB (mean = 1.48 mg L^{-1}) were significantly higher ($p < 0.001$, Kruskal-Wallis test) than for the other raised bog sites with the lowest mean concentration at RBIB (0.66 mg L^{-1}). RBR2 had the second-highest mean NH_4-N concentration (1.11 mg L^{-1}), while RBR1 (0.50 mg L^{-1}) was not significantly different from RBIB. Given that the majority of TON concentrations were below the detection limit, and NO_2-N concentrations were generally lower than 0.02 mg L^{-1}, both NO_2-N and NO_3-N are not presented. Mean PO_4-P concentrations for RBIB, RBAB, RBR1 and RBR2 were, 0.05 mg L^{-1}, 0.29 mg L^{-1}, 0.12 mg L^{-1} and 0.40 mg L^{-1}, respectively. PO_4-P concentrations at RBR2 were significantly higher ($p < 0.02$, Kruskal-Wallis test) than the other sites, and although they were less at RBR1, they were still significantly higher ($p < 0.001$, Kruskal-Wallis test) than at RBIB.
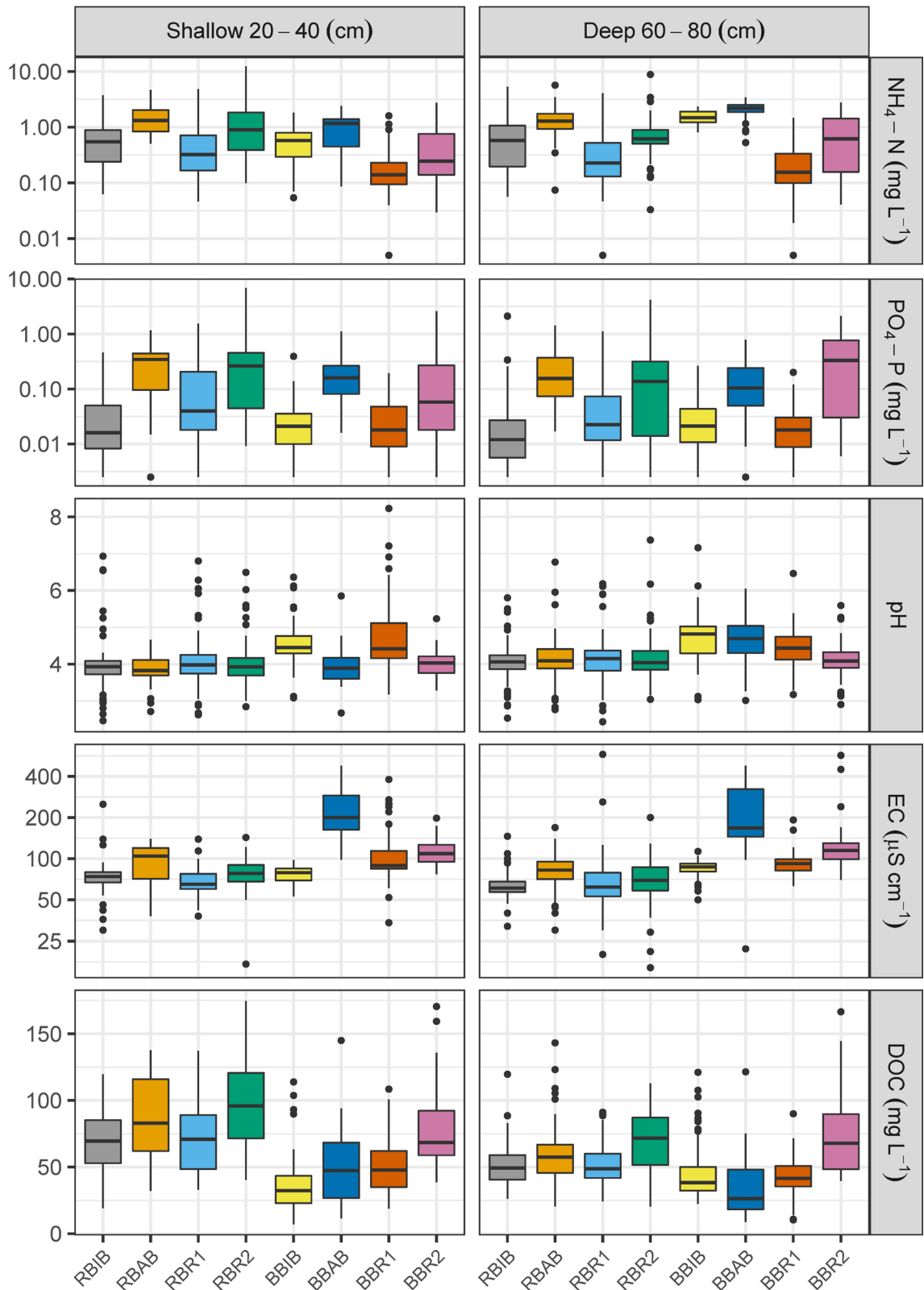
Figure 3-5 – Porewater variables for shallow and deep porewater. Log scales were used for NH₄-N, PO₄-P and EC to aid readability. RB = raised bog; BB = blanket bog; IB = intact bog; AB = afforested bog; R1 = oldest restoration site; R2 = most recent restoration site. The upper and lower limits of the boxes represent the upper and lower quartiles (25%) and the whiskers the variability outside those limits. The horizontal lines are the median, and the points represent any outliers.

There was no significant difference in the pH between the raised bog sites, although the means were fractionally higher (~0.1 units) in the two restoration sites than at RBIB and RBAB. The mean EC was 19 µS cm^{-1} higher ($p < 0.001$, Kruskal-Wallis test) in RBAB than the intact bog, but it was lower at the two restoration sites with no significant difference between RBR1 (72 µS cm^{-1}) and RBIB (69 µS cm^{-1}). Mean DOC at RBR2 (77.8 mg L^{-1}) was significantly higher ($p < 0.05$, Kruskal-Wallis test) than at RBAB (67.2 mg L^{-1}), RBR1 (58.5 mg L^{-1}) and RBIB (59.2 mg L^{-1}). On average, the E4:E6 ratio and SUVA$_{254}$ values, at 20-40 cm depths (Table 3-3), were significantly lower ($p < 0.05$, Kruskal-Wallis test) at RBAB than RBIB. However, no significant difference was found for DOC, E4:E6 and SUVA$_{254}$ between RBR1 and RBIB.

Table 3-3 – Comparison of E4:E6 ratio (unitless) and SUVA$_{254}$ (L mg^{-1} m^{-1}) means ± SE for the study sites (20-40 cm depths). RB = raised bog; BB = blanket bog; IB = intact bog; AB = afforested bog; R1 = oldest restoration site; R2 =most recent restoration site. Significant differences are taken from Kruskal-Wallis pairwise comparisons. Significance levels are denoted as: *** < 0.001; ** < 0.01; * < 0.05.

			E4:E6			SUVA$_{254}$		
Location	S1	S2	S1 Mean	S2 Mean	Sig.	S1 Mean	S2 Mean	Sig.
RB	RBAB	RBR2	6.62 ± 0.18	8.95 ± 0.30	0.000 ***	3.43 ± 0.11	3.31 ± 0.04	0.077
	RBAB	RBR1	6.62 ± 0.18	9.63 ± 0.44	0.000 ***	3.43 ± 0.11	3.39 ± 0.03	0.242
	RBAB	RBIB	6.62 ± 0.18	9.90 ± 0.31	0.000 ***	3.43 ± 0.11	3.50 ± 0.04	0.010 *
	RBR2	RBR1	8.95 ± 0.30	9.63 ± 0.44	0.192	3.31 ± 0.04	3.39 ± 0.03	0.002 **
	RBR2	RBIB	8.95 ± 0.30	9.90 ± 0.31	0.040 *	3.31 ± 0.04	3.50 ± 0.04	0.000 ***
	RBR1	RBIB	9.63 ± 0.44	9.90 ± 0.31	0.600	3.39 ± 0.03	3.50 ± 0.04	0.168
BB	BBAB	BBR2	8.23 ± 0.47	8.60 ± 0.40	0.461	3.60 ± 0.06	3.34 ± 0.03	0.000 ***
	BBAB	BBR1	8.23 ± 0.47	7.64 ± 0.24	0.438	3.60 ± 0.06	3.52 ± 0.06	0.971
	BBAB	BBIB	8.23 ± 0.47	8.42 ± 0.31	0.390	3.60 ± 0.06	3.88 ± 0.08	0.004 **
	BBR2	BBR1	8.60 ± 0.40	7.64 ± 0.24	0.108	3.34 ± 0.03	3.52 ± 0.06	0.000 ***
	BBR2	BBIB	8.60 ± 0.40	8.42 ± 0.31	0.964	3.34 ± 0.03	3.88 ± 0.08	0.000 ***
	BBR1	BBIB	7.64 ± 0.24	8.42 ± 0.31	0.060	3.52 ± 0.06	3.88 ± 0.08	0.001 **

At the blanket bog location, mean concentrations of NH$_4$-N were also highest in the afforested site (1.82 mg L^{-1}), but BBR1 (0.26 mg L^{-1}) and BBR2 (0.81 mg L^{-1}) had significantly lower ($p < 0.002$, Kruskal-Wallis test) concentrations than BBIB (1.11 mg L^{-1}). PO$_4$-P concentrations at BBR2 (mean = 0.51 mg L^{-1}) and BBAB (mean = 0.17 mg L^{-1}) were significantly higher ($p < 0.001$, Kruskal-Wallis test) than the other blanket bog sites, yet BBR1 and BBIB both had means of 0.03 mg L^{-1}. The mean pH was highest at BBIB (4.63) and lowest at BBR2 (4.07), which was significantly lower ($p < 0.001$, one-way ANOVA) than for the other sites at this location. EC was significantly higher ($p < 0.001$, Kruskal-Wallis test) at BBAB than any other study site and

significantly higher ($p < 0.001$, Kruskal-Wallis test) at BBR1 and BBR2 than BBIB. Mean DOC was highest at BBR2 (74 .2 mg L^{-1}) and lower at BBR1 (46.3 mg L^{-1}), yet a Kruskal-Wallis test showed BBR1 had significantly higher ($p = 0.001$) DOC concentrations than at BBIB (40.7 mg L^{-1}). SUVA$_{254}$ values (20-40 cm depths) at BBIB were significantly higher than all the other blanket bog sites ($p < 0.005$, Kruskal-Wallis test), and the means at the two restored sites were lower than BBAB.

There was a significant difference ($p < 0.001$, Mann-Whitney U test) in DOC concentrations between locations, with the mean concentration 31.6% higher at the raised bog. The E4:E6 ratios and SUVA$_{254}$ (Table 3-3) suggest the blanket bog peat is more humified and aromatic than that of the raised bog ($p < 0.05$, Mann-Whitney U test). Both pH and EC were also significantly higher at the blanket bog location ($p < 0.001$, one-way ANOVA and Mann-Whitney U test, respectively). Tests for the independence of the repeated measurements for the site and sampling month and variations in the porewater chemistry with the different surface features are given in Table A2-1 and Table A2-2, respectively.

3.3.3.1 Variations with sampling depth

At the raised bog, there was a negative correlation between DOC and sampling depth ($r_s = -0.375$, $p < 0.001$, $N = 548$) with significantly higher ($p < 0.001$, Kruskal-Wallis test) concentrations at shallow (20-40 cm) depths. DOC concentrations at shallow depths were significantly higher ($p < 0.001$, Kruskal-Wallis test) in RBR2 than RBIB. Higher PO$_4$-P concentrations were also observed at RBR2 at shallow depths, and they were more strongly correlated with DOC ($r_s = 0.476$, $p = 0.001$, $N = 46$) than at deeper depths. Positive correlations were observed for SUVA$_{254}$ ($r_s = 0.270$, $p < 0.001$, $N = 403$) and pH ($r_s = 0.207$, $p < 0.001$, $N = 556$) with sampling depth, and greater variability existed between sites at shallow depths. Averaged out for all sampling depths, SUVA$_{254}$ was not significantly different between sites, yet at shallow depths, it was significantly higher at RBIB ($p < 0.05$, Kruskal-Wallis test) than the other raised bog sites except RBR1. The mean pH was 0.13 units lower at RBAB than RBIB at shallow depths, with little difference when averaged for all sampling depths.

At the blanket bog location, the E4:E6 ratio was negatively correlated (r_s = -0.373, p < 0.001, N = 432) and NH_4-N concentrations were positively correlated (r_s = 0.341, p < 0.001, N=514) with sampling depth. Higher PO_4-P concentrations at BBR2 were observed at deeper sampling depths (60-80 cm), and there was a stronger positive correlation between DOC and PO_4-P (r_s = 0.497, p < 0.001, N = 79) than at shallow depths. The mean pH at BBAB was significantly (p<0.001, one-way ANOVA) lower than at BBIB at shallow depths (20-40 cm), by 0.59 units, but it was least acidic at the deepest depth (80 cm). At shallow depths, the mean pH at BBR1 was 0.65 units higher than BBR2, whereas BBR1 and BBIB were not significantly different.

3.3.3.2 Seasonal variability

Figure 3-6 shows the temporal variations in porewater chemistry at the raised bog location. There was greater seasonal variability in NH_4-N, PO_4-P and DOC concentrations at shallow depths (20-40 cm) than at deeper depths (60-80 cm). Seasonal peaks in the shallow porewater occurred most frequently at the afforested and restoration sites. Peaks were observed at RBR2 for NH_4-N in July 2019 (4.19 mg L^{-1}), PO_4-P (1.03 mg L^{-1}) in April 2018 and DOC (115.84 mg L^{-1}) in September 2019. Winter peaks at RBR2 were limited to a spike in PO_4-P (0.93 mg L^{-1}) in the final sampling month. Other near-surface porewater peaks were observed at RBIB for pH (5.68) in the first sampling month, and NH_4-N (> 2.5 mg L^{-1}) at RBAB, in the autumn.
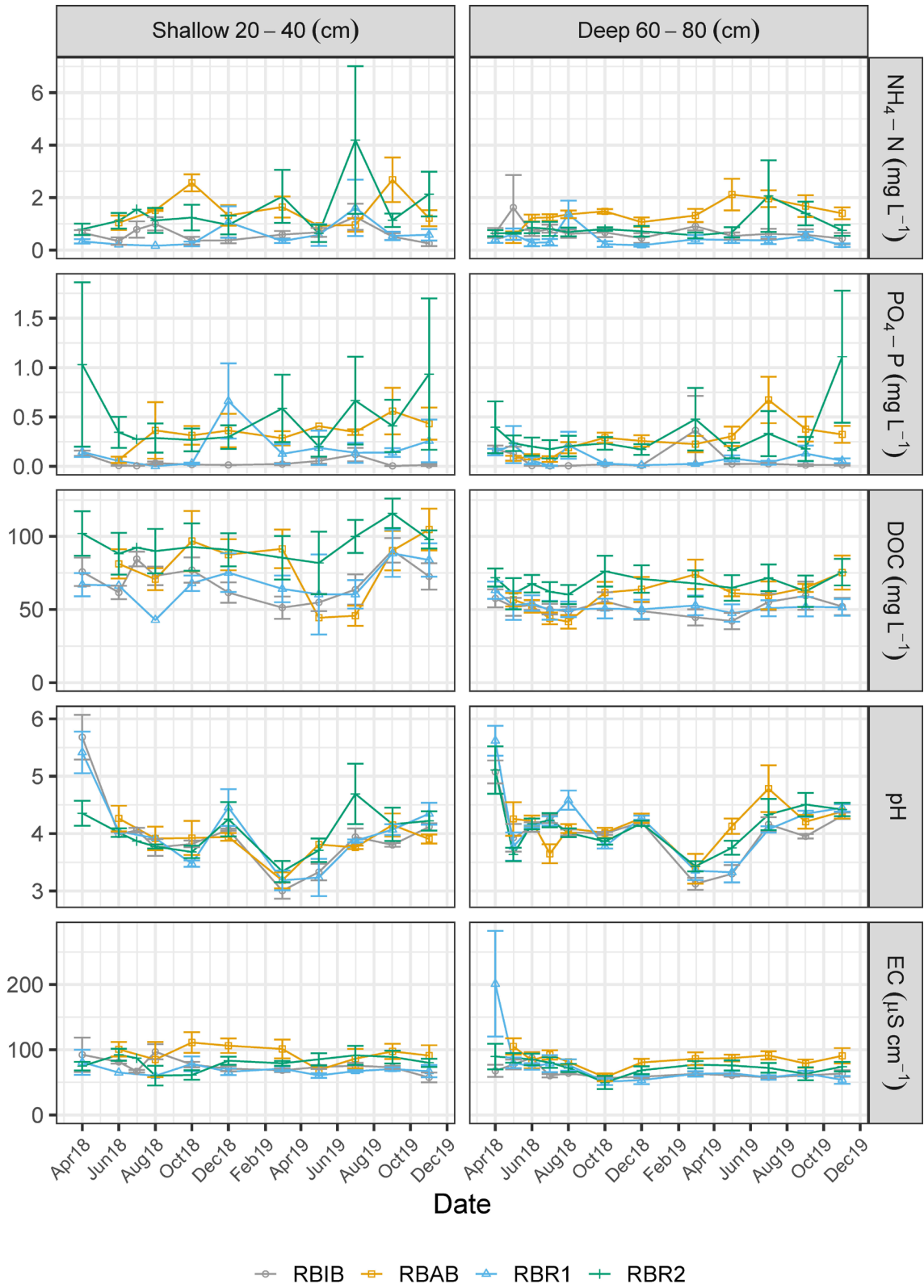
Figure 3-6 – Time series data of mean porewater concentrations ± SE for shallow and deep porewater for the raised bog location. IB = intact bog; AB = afforested bog; R1 = oldest restoration site; R2 =most recent restoration site.

Although there was less variability in the porewater solutes at deeper sampling depths at the raised bog location, they still displayed some seasonality. A peak in PO_4-P at RBR2 in the shallow porewater saw a corresponding peak (1.11 mg L^{-1}) in the deeper porewater (November 2019). Peaks in PO_4-P (0.67 mg L^{-1}) and pH (4.78) at RBAB were observed in July 2019. NO_3-N was typically present in low concentrations, but minor peaks were observed, usually in dry periods.

Figure 3-7 shows the temporal variations in porewater chemistry at the blanket bog location. BBAB experienced two peaks in NH_4-N at shallow depths in March 2019 (1.56 mg L^{-1}) and September 2019 (1.48 mg L^{-1}). At BBR2, NH_4-N peaked (shallow = 0.82 mg L^{-1}; deep = 1.50 mg L^{-1}) at the same time as PO_4-P (shallow = 0.72 mg L^{-1}; deep = 1.05 mg L^{-1}) and DOC (shallow = 101.80; deep = 81.77 mg L^{-1}) in the autumn after the dry summer of 2018. At BBAB, EC fell to 66 μS cm^{-1} in the dry period of July 2018 in the deeper porewater, rising to a peak of 285 μS cm^{-1} in the autumn of 2018 in the shallow porewater. NO_3-N was found in similarly low concentrations to the raised bog, apart from minor peaks usually associated with dry periods.

Except for BBAB, where EC was elevated beyond the other sites, seasonal patterns in pH and EC were similar at the two locations, with greater variability in pH. At both locations, the highest mean pH was recorded in April 2018 and the lowest in March 2019, with similar seasonal trends at both shallow and deeper depths. E4:E6 ratio and $SUVA_{254}$ varied little between sampling dates and are, therefore, not presented.
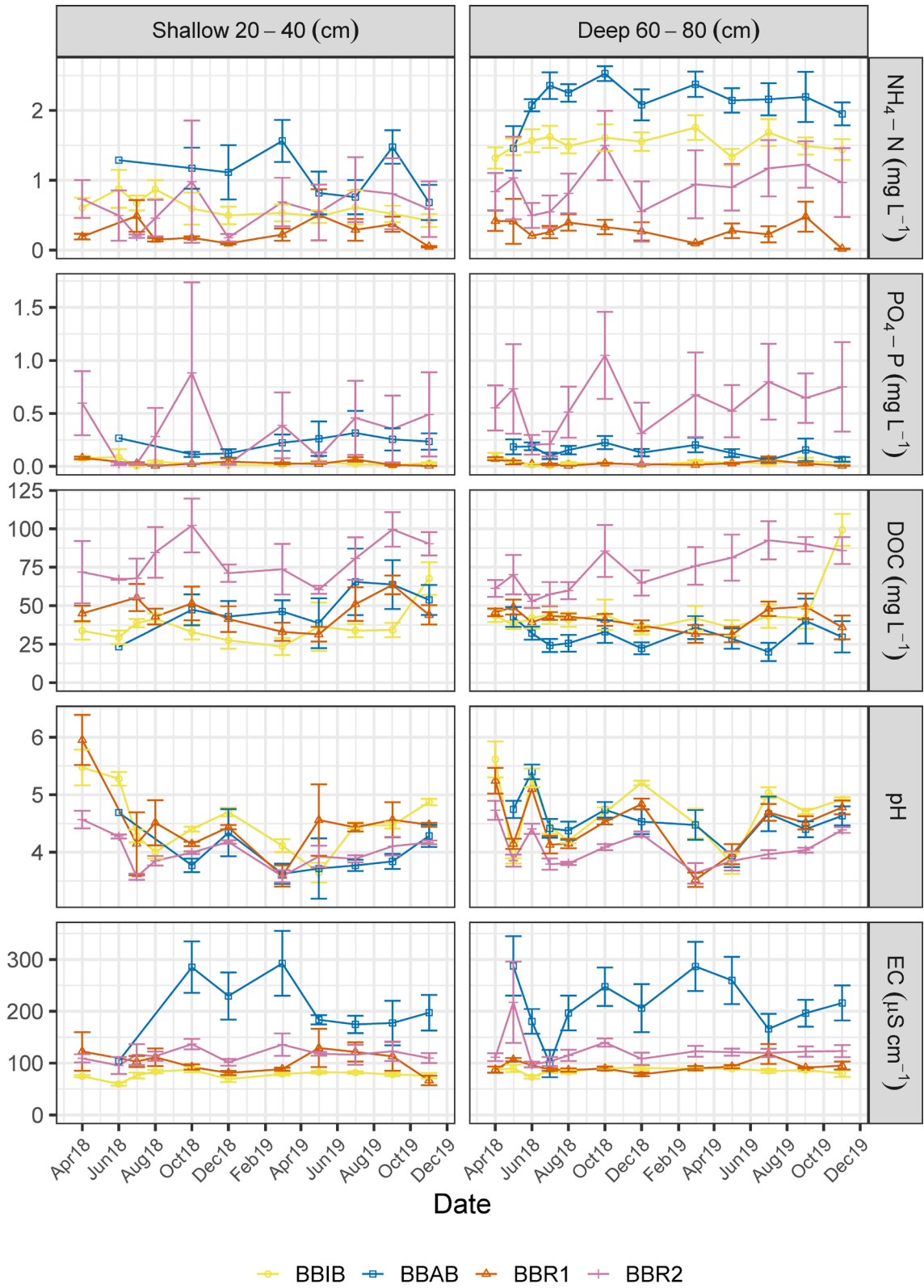
Figure 3-7 – Time series data of mean porewater concentrations ± SE for shallow and deep porewater for the blanket bog location. IB = intact bog; AB = afforested bog; R1 = oldest restoration site; R2 = most recent restoration site.

3.3.3.3 Principal component analysis

Principal component analysis (PCA) was used to highlight the associations between variables for the three treatment groups (intact, afforested, restored) at each location (Figure 3-8). NH_4-N, EC and WTD appeared to be associated with the forestry at both locations, but the associations were stronger at the blanket bog location. High concentrations of PO_4-P, NO_2-N and DOC were more strongly associated with the blanket bog restoration sites, and nests 16, 17 (RBR2) and 40 (BBR2) were consistently outside the normal probability for the clusters of observations. The chemical composition of the porewater at the raised bog restoration sites is closer to the other treatment groups, whereas, at the blanket bog, there is a distinct difference. Overall, PCA highlighted the difference in the spread of porewater observations for the afforested and restored treatment groups, with the smallest spread occurring in the intact bog at each location. However, it is important to note that measurement uncertainties can affect the outcome of PCA (Gortler *et al.*, 2020) hence the broader groupings into the three main treatment groups; afforested, intact and restored.
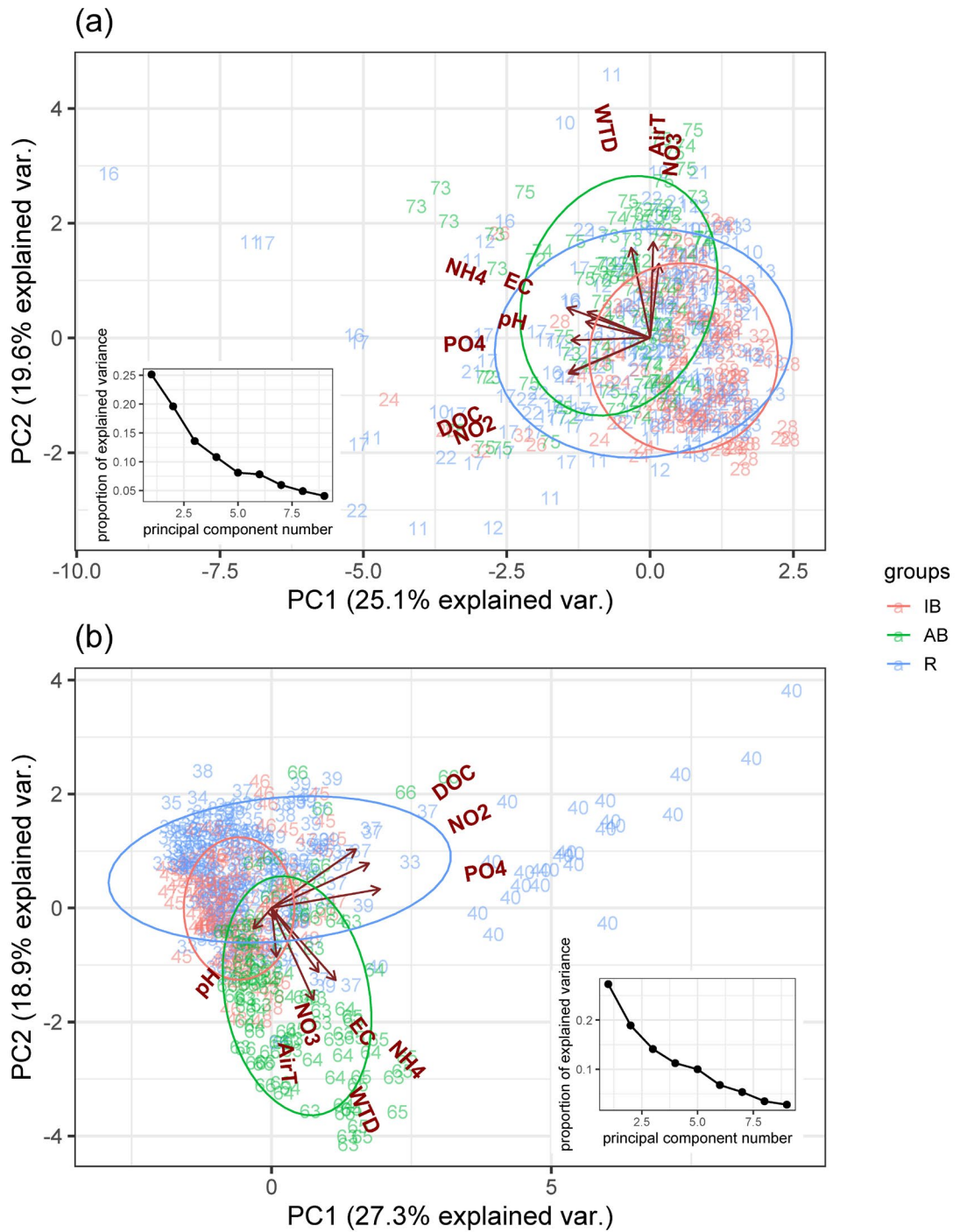
Figure 3-8 – Biplots of porewater quality at (a) the raised bog and (b) the blanket bog with respect to the first two principal components (PC). The normal range for clusters of observations is denoted by the ellipses (probability 0.68). The proportion of explained variance for each PC is plotted in the embedded scree plots. The observations are plotted with their nest labels. The closer the loadings (arrows) are to the PC axes, and the further they are from the origin indicates a higher spread of data for that PC. Arrows close together are positively correlated; arrows at 90° are uncorrelated, and those at 180° are negatively correlated.

3.4 Discussion

3.4.1 Water table

The results show that afforestation was associated with greater water-table drawdown in comparison to the intact bog for both the raised bog and blanket bog locations. The afforested sites also had significantly deeper water tables than the restoration sites. Unlike for the raised bog location, WTD in the blanket bog restoration sites was not significantly different from that in the intact bog, and where both furrows and drains had been blocked at the oldest blanket bog restoration site, we found the mean WTD was shallower than the intact bog (~17 years post-restoration) by 1.2 ± 2.1 cm. Water table recovery after forest-to-bog restoration work has been reported in other studies (Andersen *et al.*, 2017; Gaffney *et al.*, 2018; Muller *et al.*, 2015), but Gaffney *et al.* (2018) and Anderson and Peace (2017) found the recorded levels had not reached near-natural conditions. Gaffney *et al.* (2018) reported that the oldest restoration site (17 years post-restoration) where drains and not furrows had been blocked had a mean WTD that was 8 cm deeper than that of the intact sites. Gaffney *et al.* (2020) also suggest that the effects of drain blocking alone can be quite localised and had previously suggested that furrow blocking may also be required to assist water-table recovery (Gaffney *et al.*, 2018). However, the fact that the mean WTD was similar to the intact bog in both blanket bog restoration sites in this study suggests additional local factors such as slope or microtopography are also likely to be important in controlling water-table recovery following forest-to-bog restoration. It should also be noted that this study was not specifically designed to test for the effects of drain and furrow blocking on water tables.

In dry periods, the water-table drawdown at both locations was much more pronounced in the afforested than the intact bog, and the drawdown in the restoration sites was similar to the intact afforested bog. Anderson and Peace (2017) found a slight water-table drawdown in restored sites 5 m outside the former forest edge in dry conditions at a blanket bog location. Our study found higher water-table drawdown in the restoration sites compared to the intact bog during drought periods, but the drawdown effect was less for the oldest restoration sites. Outside of drought conditions, there was less

difference between the WTD in the restoration sites and the intact bog, but more difference between the most recently restored sites and those restored earlier.

3.4.2 Restoration impacts on porewater chemistry

The porewater chemistry and the PCA highlighted that higher concentrations of DOC and PO_4-P were associated with restoration, particularly at the blanket bog location. The mean PO_4-P concentration at BBR2 (0.51 mg L^{-1}) was ~3 times higher than BBAB (0.17 mg L^{-1}) and ~17 times higher than BBR1 (0.03 mg L^{-1}). PO_4-P concentrations were significantly higher at RBR2 than RBIB and RBR1 at all depths. However, at shallow depths (20-40 cm), the mean PO_4-P concentration was 0.17 mg L^{-1} higher at RBR2 than BBR2, both of which were restored at a similar time. At deeper depths, PO_4-P concentrations were higher at BBR2 than RBR2. No mineral deposits were detected in the top 1 m of peat taken from BBR2. Therefore, we are unable to explain why higher concentrations of PO_4-P at BBR2 were detected at deeper sampling depths.

Averaged across both locations, the mean concentrations of PO_4-P at the shallowest depths (20 cm) were ~10 times higher in the afforested (0.33 ± 0.07 mg L^{-1}) than the intact bog (0.03 ± 0.01 mg L^{-1}), which could be due to fallen needles and other forest litter (Asam *et al.*, 2014a; Moore *et al.*, 2005). Historical fertiliser applications may be another potential source of elevated PO_4-P concentrations, which have been found to persist in surface waters for up to 10 years (Kenttämies, 1982) and could persist for longer in porewater. However, it might be expected that the trees would have sequestered any excess P, given their relative planting dates (Drinan *et al.*, 2013). PO_4-P concentrations were often low (< 0.1 mg L^{-1}, 67.1% of the time) at most piezometer nests, but high values (> 2 mg L^{-1}) were detected in some nests (i.e. nests 17 and 40), suggesting some local effects. Nests 17 (RBR2) and 40 (BBR2) were in well-defined furrows providing preferential flow paths for runoff; these furrows contained higher forest biomass compared to other nests, suggesting that the forest biomass was the major source of PO_4-P. Furthermore, we hypothesise that the accelerated decay of the mulched material at BBR2, which would likely decompose more readily than coarser forest debris, contributed to the higher PO_4-P concentrations at this site.

Some studies on UK and Scandinavian peatlands (Asam *et al.*, 2014b; Clarke *et al.*, 2015; Kaila *et al.*, 2014; Koskinen *et al.*, 2017; Rodgers *et al.*, 2010; Shah & Nisbet, 2019) have suggested increases in porewater and surface water concentrations of PO_4-P, as a result of forestry operations, to be a relatively short-term effect (3–5 years). Others have suggested timeframes > 10 years (Gaffney, 2017; Gaffney *et al.*, 2018; Palviainen *et al.*, 2014). In this study, porewater concentrations of PO_4-P at RBR2 and BBR2 were significantly higher than the intact bog 5-6 years post-restoration. The only restoration site where PO_4-P concentrations were not significantly different from the intact bog was BBR1, 17 years after restoration. Elevated PO_4-P concentrations in the porewater may persist for longer periods than surface water from the catchment outlets studied by Shah and Nisbet (2019), with porewater concentrations at RBR1 70 $\mu g\ L^{-1}$ higher than the intact bog, 9 years after restoration. After dilution in surface waters, they are unlikely to cause concern, but the higher concentrations detected by Shah and Nisbet (2019) shortly after clear-felling suggest caution should be applied in ecologically sensitive waters (e.g. upstream of freshwater pearl mussel populations or lochs).

Other studies have reported that forest residues are a primary source of organic matter and thus nutrients and DOC (Muller *et al.*, 2015; Shah & Nisbet, 2019). Elevated DOC and PO_4-P concentrations, which may be attributed to forest residues, have been reported in both streamwater (Kaila *et al.*, 2014; Koskinen *et al.*, 2011; Koskinen *et al.*, 2017; O'Driscoll *et al.*, 2014; Rodgers *et al.*, 2010) and porewater (Asam *et al.*, 2014b; Gaffney *et al.*, 2018). Our results found a significant positive correlation between DOC and PO_4-P at RBR2 and BBR2, which was higher at the mulched site (BBR2). Other factors that influence DOC production are WTD, temperature and pH (Clark *et al.*, 2009). Lower water tables through drainage have been found to stimulate enzymes responsible for peat decomposition and increased DOC production (Peacock *et al.*, 2015). Temperature can increase DOC production directly by stimulating microbial activity within the peat (Kane *et al.*, 2014) or indirectly by increased plant productivity (Freeman *et al.*, 2004). The solubility of DOC in soil solution is widely known to increase with increasing pH (Clark *et al.*, 2005). Neither WTD nor pH proved to be a strong control of DOC in this study, although there was more variability in

concentrations at shallow depths where most of the fluctuations in WTD occurred, suggesting WTD had some influence. Despite the influence of WTD and pH on DOC, seasonal temperature changes can sometimes be more important (Koehler *et al.*, 2009). At the restoration sites, the DOC may be derived from the above-ground biomass (Don & Kalbitz, 2005) or decomposition of bare peat (Qassim *et al.*, 2014) following clear-felling. Therefore, it is likely the influence of the WTD and pH on DOC at the restoration sites is masked by the input of DOC from the tree litter or surface peat decomposition, particularly after dry periods.

As observed in other peatland restoration studies (Gaffney *et al.*, 2018; Urbanová *et al.*, 2011), the dominant form of inorganic nitrogen was NH_4-N, with low NO_3-N concentrations (Gaffney, 2017; Shah & Nisbet, 2019; Urbanová *et al.*, 2011) at both locations. Other studies have found nitrate leaching to be more of an issue in minerotrophic fens than bogs (Koskinen *et al.*, 2011; Koskinen *et al.*, 2017). Shah and Nisbet (2019) observed modest increases of NO_3-N in streamwater at the raised bog following felling, where porewater NH_4-N would be readily oxidised to NO_3-N (Daniels *et al.*, 2012) in streams, but concentrations never exceeded 0.5 mg L^{-1}.

3.4.3 Legacy effects from afforestation

Solute concentrations and principal component analysis suggested that water-table drawdown and higher EC and NH_4-N concentrations were associated with afforestation. Average NH_4-N concentrations were 0.83 mg L^{-1} higher at RBAB and 0.71 mg L^{-1} higher at BBAB ($p < 0.001$), where WTD was more drawn down than the intact bog. Our findings were similar to those of Gaffney *et al.* (2018). However, they found elevated NH_4-N concentrations after restoration persisted for > 17 years. We found significantly lower NH_4-N concentrations in the oldest restored sites at both locations than in the intact bogs. Therefore, it was not found to be a long-lasting legacy effect in this study. The deeper water table in the afforested bog may increase the mineralisation of organic matter within aerobic peat (Daniels *et al.*, 2012; Sapek, 2008), enhancing porewater concentrations of NH_4-N. Previous studies have found higher concentrations of NH_4-N in peatlands with water-table drawdown and

particularly after drainage (Daniels *et al.*, 2012; Gaffney, 2017; Gaffney *et al.*, 2018; Holden *et al.*, 2004). Furthermore, conifer trees have been found to capture 40-60% of atmospheric nitrogen deposition in the canopy (Pryor & Klemm, 2004; Schulze, 1989), and this could, to a certain extent, explain the higher NH_4-N concentrations in the afforested bog.

EC was significantly higher at the blanket bog location, particularly at BBAB, which is likely a consequence of being nearer the coast. Forest scavenging of sea salts has been reported in other studies (Dunford *et al.*, 2012; Monteith *et al.*, 2007), and surface water from a nearby forest drain was found to contain significantly higher Na^+ and Cl^- concentrations than all the other sites in the study, which supports this argument. Therefore, the significantly higher EC observed at BBR1 and BBR2 compared to the intact bog is likely a legacy effect of sea-salt scavenging from the former forestry. The effect was less noticeable on the raised bog, which was further inland in comparison, but EC was significantly higher at RBAB than the other raised bog sites.

3.4.4 Differences between location

Overall, the water-table comparisons between restored, afforested and intact sites between the raised bog and the blanket bog in this study appear similar. However, there was a closer correspondence in water table between the restored and intact blanket bog sites than those at the raised bog, despite the lower annual rainfall at the blanket bog location. Therefore, the fact that the trees were less mature at the blanket bog location, coupled with the blocking of the drains at both restoration sites and furrows at BBR1, would likely explain why the water table at the blanket bog restoration sites was more similar to the intact bog. Prolonged water-table drawdown at the raised bog as a result of afforestation may have led to more peat degradation, providing new voids and pathways for flow within the peat, and greater hydrophobicity (Holden & Burt, 2002; Worrall *et al.*, 2007), which could all account for a potentially slower recovery in WTD at the restoration sites at the raised bog compared to at the blanket bog location.

The mean DOC concentration was 15.7 mg L^{-1} higher in the raised bog than the blanket bog. Other studies have reported very high porewater DOC concentrations in raised bogs (Grau-Andrés *et al.*, 2019) which could be due to the higher plant productivity and warmer climatic due to their lowland setting (Freeman *et al.*, 2001; Freeman *et al.*, 2004) or the relative immobility of DOC (Glatzel *et al.*, 2019). Elevation and air temperature differences were not strong, but the blanket bog was significantly cooler (*p* < 0.001, one-way ANOVA) than the raised bog over the study period. Therefore, the higher DOC in the raised bog could be through higher temperatures stimulating plant, microbial and enzyme activity (Kane *et al.*, 2014) and the significantly deeper WTD in the raised bog. DOC may also be less concentrated in the porewater of the blanket bog system due to the greater mobility of solutes (Glatzel *et al.*, 2019). Mean SUVA$_{254}$ values for the sites also suggested DOC was naturally more hydrophobic at the blanket bog location. The E4:E6 ratio and SUVA$_{254}$ values were closer to the intact site at the raised bog location, suggesting that DOC quality may have been quicker to respond to restoration in terms of lability and degree of humification than at the blanket bog sites. However, these results and lower variability in solute concentrations between the raised bog sites are unexpected, given the greater variability in WTD compared to the blanket bog.

3.4.5 Implications for management

The results of this study have several important implications for management. However, it is important to note that we did not undertake a before-after time-series approach with each site and to note that the restoration methods differed between the two locations, local environmental conditions may have affected the results, and the sites were restored at different times. Management implications include:

i. For both the raised and blanket bogs, porewater DOC and PO$_4$-P concentrations were significantly higher at the most recently restored sites than the afforested and the intact bog. The increases in DOC and PO$_4$-P are most likely related to leaching from forest residues and soil disturbance following clear-felling. Therefore, to ensure forest-to-bog restoration has minimal impact on water quality, we suggest clear-felling of the trees is carried out in phases to reduce the likelihood of high peaks in PO$_4$-P, particularly for large sites.

ii.   Given that WTD was most similar to the intact bog in the restored sites where drain and furrow blocking had taken place, and the fact Gaffney *et al.* (2020) reported drain-blocking to have a localised impact on WTD, this suggests that both drains and furrows should be blocked to encourage more rapid water-table recovery for whole forest blocks.

iii.   We observed that PO_4-P concentrations were between two and five times higher in porewater taken from furrows and drains in which brash had accumulated, either deliberately as part of the restoration or naturally than from other locations at the same sites where it had not. Therefore, we recommend that brash is not allowed to accumulate in furrows or drains and that, ideally, it is removed from forest-to-bog restoration sites.

iv.   The highest concentrations (mean = 0.51 mg L^{-1}) of porewater PO_4-P were observed at BBR2, where the trees had been mulched, and the material spread over the site. The highest porewater DOC concentrations (mean = 74.2 mg L^{-1}) for the blanket bog were also observed at this site. These results suggest that mulched debris is a major source of water-soluble C and PO_4-P, leached from drainage waters mixing with the fresh/senescent forest biomass and transferred from the vegetation to the peat and subsequently surface waters (Wickland *et al.*, 2007). However, a focused study on the impacts of mulching with replication would be necessary to fully determine the effects on porewater and surface water.

3.5 Conclusions

We found significant differences in the WTD and porewater chemistry between intact, afforested, and restored bog sites at both the raised bog and blanket bog locations. Forest-to-bog restoration sites were associated with much shallower water tables than afforested sites, and WTD was closest to near-natural conditions in the blanket bog restoration sites where drain and furrow blocking had taken place. Elevated porewater concentrations of NH_4-N, higher EC and deeper WTD are more associated with the afforested bog at both locations. In contrast, elevated porewater concentrations of PO_4-P and DOC are more associated with the restoration processes and the impact of clear-felling. There were few differences in porewater chemistry between intact bog and the oldest restoration sites in this study. However, PO_4-P concentrations were significantly higher at the raised bog site that had been restored nine years earlier than in the nearby

near-natural bog. For the blanket bog system, DOC concentrations and EC were significantly higher in the site, which had been restored 17 years earlier than the intact bog. Elevated porewater PO_4-P concentrations were found where brash had accumulated in drains and furrows and where forest materials were mulched on site. Therefore, we recommend that brash is not allowed to accumulate in furrows or drains and that, ideally, it is removed from restoration sites to reduce the impact of forest-to-bog restoration on downstream water quality.

3.6 Acknowledgements

3.7 References

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Chapter 4: The effect of forest-to-bog restoration on the hydrological functioning of raised and blanket bogs

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Abstract

The carbon sequestration potential of peatlands has led to increasing interest in restoring bogs previously subjected to plantation forestry. However, little information exists about the effects on hydrological processes of what has become known as forest-to-bog restoration. The hydrological functioning of three afforested, two intact and four forest-to-bog restoration sites was compared at a raised bog and blanket bog location. For the raised bog location, the annual runoff/rainfall coefficient was 59.7% for the intact site, 41.0% for the afforested site, and 53.1% for the oldest restoration site (9 years post-felling). At the blanket bog location, the coefficient was 80.6% for the intact site, 63.0% for the afforested site, and 71.6% for the oldest restoration site (17 years post-felling). Compared to intact bog, median peak storm discharge was significantly greater in the restoration sites for the raised bog location but not for the blanket bog location. Water-table peak lag times were greatest, and water-table depths were deepest in the afforested sites and the most recent raised bog restoration site and least in the oldest blanket bog restoration site. The estimated contribution of overland flow in the afforested sites was 2.9% for the raised bog and 11.9% for the blanket bog, increasing to 8.7% and 32.2% at the oldest restoration sites for the raised bog and blanket bog, respectively. Overall, hydrological functioning of the raised bog and blanket bog restoration sites was different from the intact sites but was most similar to the intact bog in the oldest restoration sites.

4.1 Introduction

Globally, peatlands are now widely recognised for their potential to mitigate climate change through carbon sequestration (Scharlemann *et al.*, 2014; Yu *et al.*, 2010). In the boreal zone, more carbon is thought to be stored in peat soils than in the above-ground biomass, including natural forests (Apps *et al.*, 1993). Peatlands also provide a range of other important ecosystem services, including nature conservation (Stoneman *et al.*, 2016), freshwater supplies (Xu *et al.*, 2018) and downstream flow maintenance, influencing flood events (Acreman & Holden, 2013). However, peatlands are complex and fragile ecosystems, and many have been impacted by industrial development through changes in land use, air quality and global climate. A tightly-coupled feedback system exists between the peat, the native vegetation and the hydrology (Price *et al.*, 2016), and a suitable balance is required to sustain carbon sequestration via continuous accumulation of new peat in these ecosystems. Changes in land use and climate can disrupt this balance, altering the hydrology and the ecosystem services delivered.

Bogs are ombrogenous peatlands, being predominantly rain-fed. Blanket bogs occur where the underlying topography becomes covered in an extensive layer (blanket) of peat, and they can occur on sloping (up to 20º) or flat terrain. Raised bogs usually occur on more gentle slopes and form a characteristic dome shape with deeper peat in the centre of the peatland (Charman, 2002). Hydrology is very important to the functioning of bogs. Near-surface water-table levels in bogs are widely regarded as the most crucial factor in maintaining the anoxic conditions necessary for peat accumulation (Holden *et al.*, 2015; Joosten *et al.*, 2016), as they slow down decomposition (Clymo, 1983). Also, high water tables maintain the growth of peat-forming plants such as *Sphagnum spp*. and *Eriophorum spp*. (González *et al.*, 2014) which sequester carbon from the atmosphere.

The flow of water in both intact raised bogs and intact blanket bogs is dominated by near-surface and surface pathways (Holden & Burt, 2003a; Ingram, 1982; van der Schaaf, 1999). Water received by precipitation either flows across the surface of the peat as overland flow or as subsurface flow through the shallow peat layers. In contrast,

limited flow usually occurs in the denser, deeper layers except where there are macropores and soil pipes (Holden and Burt, 2003b). Saturation-excess overland flow has been found to contribute up to 82 % of streamflow in an intact upland blanket peatland in the UK (Holden & Burt, 2003a; Holden & Burt, 2003b). However, drainage of peatlands to improve the land for grazing and forestry, burning, and other disturbances have been shown to reduce the dominance of overland flow and increase subsurface flow (Acreman & Holden, 2013; Holden *et al.*, 2006; Holden *et al.*, 2015; Prévost *et al.*, 1999) so that the hydrological functioning of a disturbed peatland is quite different from that of an intact one.

Afforestation has been a significant source of peatland degradation throughout the world (Paavilainen & Päivänen, 1995; Strack, 2008), and concern over the changing climate has led to a global increase in peatland restoration (Andersen *et al.*, 2017; Bonn *et al.*, 2016) including restoration of peatlands that have previously been subject to plantation forestry (Anderson *et al.*, 2016). In the UK, 190000 hectares of deep peat was ploughed and planted with non-native coniferous trees between the 1950s and 1980s (Hargreaves *et al.*, 2003). Due to the naturally shallow water tables found in deep peat, artificial drainage was necessary to allow the trees to establish. Drainage and increased evapotranspiration from trees can significantly lower the water table (Anderson & Peace, 2017; Anderson *et al.*, 2016; Gaffney *et al.*, 2018; Muller *et al.*, 2015), reduce water yield and subdue streamflow response to rainfall (Bosch & Hewlett, 1982; Brown *et al.*, 2005; Sahin & Hall, 1996; Zhang & Wei, 2014). However, in some cases, drainage can provide a more efficient pathway for flow, particularly in the early stages of a forest rotation, enhancing water yield and streamflow response (Holden *et al.*, 2004; Robinson, 1986). Many coniferous plantation forests on peatlands in the UK are now reaching maturity, and more information is needed to understand the impacts of land management decisions such as felling and restocking or peatland restoration under 'forest-to-bog' initiatives (Anderson *et al.*, 2016) on the hydrological functioning of different bog types.

Robinson (1986) found forest drainage of the Coalburn catchment in Northumberland, northern England, led to a doubling of baseflow and an increase in annual streamflow by 50-100 mm after the ploughing of peaty soils. In the first five years after the trees were planted, mean storm peak lag times were reduced from 2.2 to 1.7 hours (Robinson, 1998). However, higher evapotranspiration rates as the trees matured and the infilling of drains with sediment, forest litter and vegetation reversed these effects with time. After 45 years, annual streamflow was 350 mm lower than before forestry operations began, although there was only a small difference in water yield for large storms (Birkinshaw *et al.*, 2014). Anderson *et al.* (2000) found baseflows to decrease and total annual streamflow to be reduced by 7% five years after afforestation in deep peat at Bad a' Cheo, Caithness, but the control in the study had also been drained. Other field studies on the hydrological effects of afforestation on peatlands have been undertaken (Archer, 2003; Bathurst *et al.*, 2018; Robinson *et al.*, 2003; Robinson *et al.*, 2013), yet only two paired catchment studies have used a near 100% afforested and near 100% open peatland as a comparison (Bathurst *et al.*, 2018; Marc & Robinson, 2007). Both studies reported smaller total annual streamflow (18 and 24%, respectively) in the afforested catchments relative to open peatland.

Forest harvesting has been associated with changes in streamflows. Sahin and Hall (1996) found that a 10% reduction in coniferous forest increased the annual water yield by 20 - 25 mm from a regression analysis of 145 catchments worldwide. However, such studies in peatland systems are not common. Robinson *et al.* (2003) noted that forest felling in deep peat at Glenturk in Ireland increased moderate peak flows, and there was a tendency for flow peaks and low flows to increase after partial felling at Plynlimon, Wales. However, Robinson *et al.* (2003) found changes in peak flows difficult to detect, which they suggested could be because of increased interception losses from the felled waste, which may also act like dams in furrows and drains attenuating runoff. It is unclear how long is required for the hydrological functioning of sites that have been felled and left to rehabilitate naturally, return to that of intact peatlands, or whether other restoration measures such as ditch blocking can reduce the time span required. Furthermore, to our knowledge, the wider impact of forest-to-bog

restoration on storm runoff, streamflow regimes and downstream flooding has not been studied.

Clear-felling alone may not raise the peatland water-table level sufficiently toward that of intact peatlands in the short term. Therefore, restoration after forest clearance often includes the damming or infilling of furrows and drains (Anderson & Peace, 2017; Haapalehto *et al.*, 2011; Laine *et al.*, 2011). Water-table recovery following felling and ditch blocking has been reported for blanket bogs (Anderson *et al.*, 2000; Anderson & Peace, 2017; Gaffney *et al.*, 2018; Muller *et al.*, 2015) and raised bogs (Haapalehto *et al.*, 2011; Komulainen *et al.*, 1999; Menberu *et al.*, 2016). However, we are not aware of a published forest-to-bog restoration study on hydrological function for raised bogs in the UK. Additionally, there is limited understanding of how peatland water-table variability and water-table response to rainfall events differs between forest-to-bog restoration sites, afforested sites and intact sites. Holden *et al.* (2011) found that the water-table dynamics of a restored blanket bog where ditch blocking had occurred at a non-forested site was quite different from that in nearby intact bog six years after restoration. We are only aware of one restoration study (Menberu *et al.*, 2016) that has reported the water-table dynamics in afforested peatlands, comprising the infilling of drainage ditches, construction of peat dams and surface barriers, and tree removal if significant growth had occurred since drainage. Menberu et al. (2016) observed water-table depths, fluctuations, hydrograph recession slopes, and measures of groundwater recharge reflected those found in natural peatlands 1-6 years after rewetting, particularly for nutrient-poor spruce mires. However, they did not specify whether felling had contributed to the recovery.

This study seeks to compare the hydrological functioning of nearby intact, afforested and forest-to-bog restoration sites at a raised bog and blanket bog location. We compare the water balance, streamflow dynamics, water-table dynamics and overland flow occurrence between the different sites. We hypothesise that for each of the two types of peatland (raised bog and blanket bog), the water yield would be greatest for the intact bogs, followed by the restoration sites and least for the afforested bogs. We also hypothesise that water tables would be deepest in afforested sites and deeper and

more variable in the restoration sites after clear-felling than for intact bog. As a result, overland flow was expected to be least common on forested sites, followed by the restoration sites and then intact sites. Furthermore, we hypothesise that streamflow storm response would be more subdued (smaller peaks, longer lag times) in afforested sites, followed by restoration sites, than for intact systems. Finally, we hypothesised that sites that had been under restoration the longest would have hydrological functioning that was most similar to intact bogs compared with sites where the restoration was most recent.

4.2 Methods

4.2.1 Study sites

The raised bog (RB) location is situated at Flanders Moss, in the floodplain of the River Forth, Central Scotland (Figure 4-1), one of a series of lowland raised bogs formed by the uplifted former estuary of the river (56° 08'10.5"N, 4°19'28.7"W). The blanket bog (BB) location is at Forsinain, in the 'Flow Country' region of northern Scotland (58°25'35.6"N, 3°52'09.1"W), Europe's largest expanse of blanket peat (c. 4000 km^2). The mean annual precipitation between 1981 and 2010 (Met Office *et al.*, 2018) was 1443.7 mm at Flanders Moss and 1096.9 mm at Forsinain. The mean annual air temperature was 8.7 °C at Flanders Moss and 7.4 °C at Forsinain over the same period.

Closed canopy coniferous forestry plantation sites (afforested bog (AB)), open, near-natural bog (intact bog (IB)) and two forest-to-bog restoration sites of different ages (R1 and R2) were included to represent the different land uses. R1 was the oldest restoration site at each location, although the method and timescale of restoration varied between sites and locations (Table 4-1). There were two afforested sites at Flanders Moss as, after the first site was instrumented (RBAB1), osprey nesting (protected species) restricted access throughout the study period, so a second site (RBAB2) was established. The slopes at each site were broadly comparable, and afforested sites were selected where the whole area was under tree cover.

Table 4-1 – Site characteristics at Flanders Moss (RB) and Forsinain (BB).

Site	Description	Felling Dates	Deforestation and Re-wetting Actions	Furrow Spacing (m)	Catchment Area (ha)	Outflow Location	Planting year
RBAB1	Cardross Moss afforested bog (AB)			1.4	0.7	56°09'48.0"N 4°17'03.5"W	~1965
RBIB	Flanders Moss intact bog (IB)				6.0	56° 9'47.00"N 4°10'52.29"W	
RBAB2	Flanders Moss afforested bog (AB)			1.4	0.2	56° 9'10.12"N 4°20'1.54"W	~1965
RBR1	Flanders Moss restoration site 1 (R1)	24/11/2009 - 09/12/2009 01/08/2011 - 18/10/2011	Part conventional harvesting; part low impact harvesting and removal of brash and logs.	1.4	2.5	56° 8'12.88"N 4°19'35.19"W	~1965
RBR2	Flanders Moss restoration site 2 (R2)	01/10/2013 - 31/03/2014	Conventional harvesting (i.e. fell, debranch, extract timber, leave brash).	1.4	26.2	56° 8'27.24"N 4°19'19.27"W	~1965
BBIB	Forsinain intact bog (IB)				1.6	58°25'10.32"N 3°51'41.01"W	
BBAB	Forsinain afforested bog (AB)			1.9	5.1	58°25'30.85"N 3°52'14.67"W	~1980
BBR1	Forsinain restoration site 1 (R1)	2002-2003	Originally felled-to-waste – furrows & collector drain blocked. Brash compressed into furrows.	1.4	1.6	58°25'58.49"N 3°51'18.76"W	~1980
BBR2	Forsinain restoration site 2 (R2)	2014-2015	Mulched – collector drain blocked.	2.3	2.3	58°25'32.21"N 3°51'44.25"W	~1980

RBAB2 and the raised bog restoration sites are located on what is known as 'Flanders Moss West', whereas the IB site is located on Flanders Moss National Nature Reserve to the east. RBAB1 is located to the northeast of Flanders Moss West in an area known locally as 'Cardross Moss'. Flanders Moss West was drained in the 1920s to improve conditions for grouse shooting, and in the 1960s and 1970s was planted with lodgepole pine (*Pinus contorta*) and Sitka spruce (*Picea sitchensis*). RBAB1 had been planted with the same mixture of tree species as Flanders Moss at a similar period, although the catchment was dominated by mature lodgepole pine. We include data from RBAB1 in this paper because nearby forest operations limited the choice of the catchment area for RBAB2, and equipment problems arose trying to measure the flows at RBAB2. We included RBAB2 in the study so that we could investigate overland flow and water-table dynamics data that we could not regularly sample from RBAB1 because of site access restrictions described above.

RBIB represents the best example of near-natural bog in the area with a mosaic of *Sphagnum* mosses (including some nationally scarce species: *S. austinii*, *S. fuscum* and *S. molle*), sedges, ericaceous shrubs and sundews. RBR2 is the larger of the two restoration catchments at Flanders Moss and was felled over six months between 2013 and 2014 using a conventional harvester and forwarder (Shah & Nisbet, 2019). The main tree stems were extracted from the site, but lesser tree debris (brash) was left to decompose on the peat surface or in furrows and drains. RBR1 was felled in two phases: the first in the winter of 2009 (15%) and the remainder in summer/autumn 2011. The first phase of felling was carried out using standard forest harvester and forwarder techniques, whereas the second phase was carried out by hand and winching the timber out by an overhead Skyline (Shah & Nisbet, 2019). All useable timber and brash were removed from RBR1. No other peatland restoration work took place in the catchments during the monitoring period, although drain blocking and other re-wetting treatments are scheduled for this site.

The vegetation at BBIB was similar in composition to that at RBIB with the addition of liverworts, bog asphodel (*Narthecium ossifragum*) and bogbean (*Menyanthes trifoliata*) in natural pools. At the southern end of BBIB, there was evidence of prior peat cutting,

and trees had been planted to the east and west, but mainly it is a good example of near-natural bog, typical to the area. In the 1980s, parts of Forsinain were drained and planted with the same mixture of tree species as the Flanders Moss, but there was a difference in the ploughing/planting phase with the furrows being 50 and 90 cm further apart in BBAB and BBR2, respectively. BBR2 differed from the other restoration sites because it was the only one where the standing trees had been 'whole tree mulched' as harvesting the timber was not economically viable, resulting in a layer of masticated tree debris being left on the peat surface. The main drain at BBR2 had been blocked with a sequence of plastic piling dams at the outflow after mulching in 2014, but further peat dams were added on 23 March 2019, 12 months after monitoring had started in the catchment. BBR1 was originally felled-to-waste in 2002-03 when the trees were comparatively young (~20 years old). The resulting brash was compacted into the furrows, which were blocked with peat dams in 2015-16 at the same time as the main collector drain.
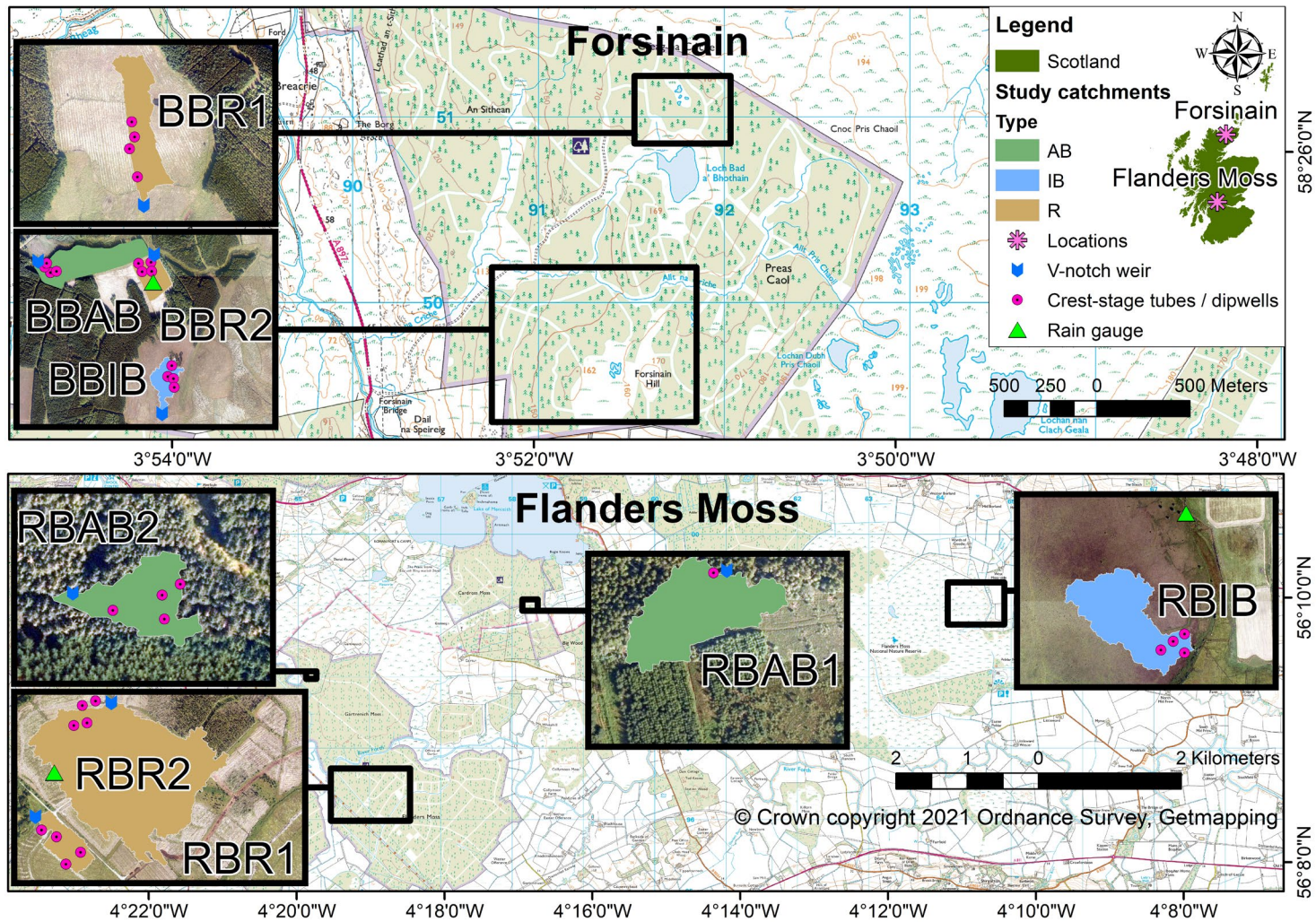
Figure 4-1 – Study site experimental design at the blanket bog (BB) and raised bog (RB) locations; AB = afforested bog; IB = intact bog; R = under restoration where R1 was restored before R2.

4.2.2 Field sampling and measurements

Within each site, four sampling nests were created, each comprising one dipwell and one crest-stage tube, which were carefully inserted into the peat after a hole had been augured of a slightly smaller diameter to the tubes. A stratified random sampling procedure was used to allocated locations within each site, using the "Create Random Points" tool in ArcGIS (ESRI, 2017). One of each of the natural bog microforms (hollows, hummocks and lawns) and one of each of the afforested and restored bog surface features (ridges, furrows and original surface) were included in the designated nest locations. The distance between the nests was generally > 30 m. The different surface features associated with afforestation and natural bog microforms including hollows ($n = 2$), hummocks ($n = 3$) and lawns ($n = 3$) in the intact bogs, and ridges ($n = 2$), furrows ($n = 8$), and the original surface ($n = 14$) in the afforested and restored bogs and vegetation were recorded at the time of installation. The dipwells were constructed from PVC tubing, generally > 1 m in length and with 0.5 cm diameter holes drilled at 3.5 cm intervals throughout the length of the tube with four holes at each interval. The base was sealed with a PVC plug. Caps were fitted to the tops of both crest-stage tubes and dipwells to prevent debris and insect ingress. The crest-stage tubes were formed from a short section of PVC tubing with a single ring of 0.5 cm diameter holes inserted so that they were level with the top of the peat layer to collect any overland flow. On each site visit, the crest-stage tubes were examined for evidence of overland flow occurring between visits, recording a presence/absence, and then emptied with a plastic syringe. Each site had four dipwells and four crest-stage tubes except where extra dipwells were added in furrows ($n = 3$), and the original surface ($n = 2$) at RBR2 and in hollows ($n = 3$) and hummocks ($n = 2$) at RBIB for further manual measurements to assess spatial variability. Manual dipwell measurements were taken with a steel capillary tube with a self-adhesive scale attached from April 2018 – November 2019, a month after the installations were complete.

Two tipping bucket rain gauges were installed at Flanders Moss (RBR2: Davis 7852 + Hobo H07-002-04 event logger; RBIB: Davis 6465 + Hobo UA00364 temperature/event logger) to account for any localised rain showers between the sites. A single tipping bucket rain gauge was installed at Forsinain, where the sites were relatively close to each other (BBR2: Davis 6465 + Hobo UA00364 temperature/event

logger). All rain gauges measured 0.2 mm of rainfall for every event recorded by the loggers. The Hobo sensors were installed in the rain gauge housing, so Met Office temperature data was used for more accurate air temperature readings. One dipwell at each site was instrumented with a Level Troll 500 vented pressure transducer (in lawns or the original lawn surface) to record high-temporal water-table measurements (every 15-minutes), except RBIB, RBR2 and RBR1, where there were two instrumented dipwells at different periods in the study. Where a single dipwell was used, we assumed that spatial differences in the water-table depth would be insignificant compared to the differences between the different land uses, particularly as lawns were consistently used for the datalogger wells. Data were collected between November 2017 and December 2019, but the synchronised monitoring of all catchments occurred between July 2018 and October 2019.

The catchment areas for each site were delineated in ArcGIS (ESRI, 2017) using high-resolution LiDAR imagery (50 cm x- y resolution except RBIB, which was 1 m resolution). V-notch weirs were installed at the outflows of the catchments with a 30° angle to capture a broad range of water levels passing through the notch for calibration purposes. The weirs were constructed from 5 mm thick aluminium sheet and machined, so there was a sloping bevel at approximately 60° on the front face of the V. The aluminium sheets were held in place by wooden fencing posts driven into the peat. A stilling well was attached to another fencing post in the stream channel behind the weir with a flush fitting cap to prevent unwanted ingress. Level Troll 500 vented pressure transducers were lowered into the stilling wells and allowed to rest on the stream bed. Each pressure transducer was set to log at 15-minute intervals, and they were all synchronised. The RBR2 catchment outlet was close to the stream's junction with the River Forth, which occasionally backed up into the catchment, affecting the head level at the weir.

On each site visit, water-table depth was recorded manually, using a steel capillary tube with adhesive scale, at each dipwell. Manual measurements were also used to calibrate the dipwells, which had been instrumented with pressure transducers. Similarly, the V-notch weirs were manually calibrated by measuring the time for water falling over the

crest to fill a known volume of a receptacle (Figures A3-1 and A3-2) when site access was permitted. A camera was secured next to the shallowest weir (RBR1) to monitor site conditions remotely and record any overtopping events that may occur throughout the study period.

RBIB was the only site that did not have a well-defined outflow channel, and there was little surface flow except in the wettest periods at the catchment outlet. However, there was a clearly defined catchment determined from the LiDAR imagery. The near-surface discharge at RBIB was therefore calculated using the groundwater flow method based on Darcy's law. The law states that discharge through a porous medium is equal to the hydraulic gradient multiplied by the hydraulic conductivity and the cross-sectional area. The saturated hydraulic conductivity (K_s) was measured using piezometer slug tests in which the time taken for the hydraulic head to recover to equilibrium after a fixed volume is removed or added is measured (Baird *et al.*, 2008; Baird *et al.*, 2004; Surridge *et al.*, 2005). Saturated hydraulic conductivity was measured near the catchment outflow at 20, 40, 60 and 80 cm depths and the cross-sectional area was calculated from the width of the lower end of the catchment, delineated in ArcGIS, multiplied by the average peat depth (assuming a uniform depth). Precisely machined piezometers were used for the slug tests with slotted 10 cm intakes and an inner tube diameter of 2.9 cm, similar to the piezometers featured in Baird *et al.* (2004), but with 3cm longer intakes to measure over a ± 5 cm depth range. The hydraulic gradient was measured continuously between two instrumented dipwells within the catchment by calculating the difference in hydraulic head divided by the distance between the two dipwells. Since there was a clearly defined catchment from the LiDAR imagery, TOPMODEL provided a good model to predict discharge from the rainfall in this catchment using the topographic index calculated from the Digital Elevation Model for the catchment at the previously mentioned scales. TOPMODEL simulations were run in R (Buytaert, 2018), supplying it with an initial value of subsurface flow (calculated by Darcy's law), the surface hydraulic conductivity and rainfall measurements to estimate the discharge over the study period, including the overland flow and subsurface flow components. Simulations were also run for the other

catchments to estimate the overland flow contribution by inputting TOPMODEL with the streamwater observations from those sites.

4.2.3 Data analysis

All time-series data were processed in R Studio (RStudio-Team, 2016), and the Kalman filter (Helske, 2017) was applied to water-table data to smooth it for seasonal display purposes. Any calculations were performed on the raw data. Annual water balance summaries were produced from the precipitation and discharge data for each catchment, and annual storage change was calculated from the water-table fluctuations and laboratory measurements of the specific yield from Chapter 2. Runoff/rainfall coefficients were calculated from the total discharge (mm) and total rainfall (mm) for each catchment over the water year 1 October 2018 – 30 September 2019 and for the entire study period 27 November 2017 – 3 December 2019 (Table A3-1). The closest weather stations with continuous air temperature records over the study period were Bishopton, Glasgow (27.3 km), and Kinbrace (17.5 km), for Flanders Moss and Forsinain, respectively. Actual evapotranspiration (AET) was estimated by subtracting the total discharge from total rainfall viewed within the context of the storage change calculations outlined above.

The baseflow index (BFI), defined as the ratio of baseflow to total stormflow over a given period, was calculated using a Lyne and Hollick (1979) derived baseflow filter (α = 0.975) produced by Bond (2019). Flow duration curves were plotted from quantile-quantile plots of the base-10 logarithm of discharge, at 15-minute intervals, divided by mean discharge using ggplot2 for each stream. "stat_qq" and "qnorm" were used for the quantile-quantile plots and calculating the percentage exceedance axes breaks, respectively. A constant of 1 was added to allow base-10 logarithms to be calculated when discharge was zero. The discharge was divided by the mean over the whole time series to compensate for the different catchment sizes.

Storm discharge metrics were calculated by processing precipitation and discharge data from a synchronised time series for each site. The 90% quantile of discharge was taken to extract the significant storm events, and a baseflow separation algorithm ($\alpha = 0.95$) was used to determine where the quickflow component was zero to signify the start and end of storm events (Fuka *et al.*, 2018). Any storm events that had missing rainfall or other anomalies which would impact on the calculated metrics were discarded ($< 5\%$), but all streamflow measurements were included. Peak discharge, the time from peak rainfall to peak discharge and the time from peak discharge to where the quickflow had returned to zero were computed to compare storm hydrographs between sites. The hydrograph intensity, used as an indication of flashiness, was also calculated by dividing the peak flow by the product of total storm discharge and a scaling factor of 10^{-6}.

Water-table storm metrics from the instrumented dipwells were calculated similarly to the storm discharge metrics without the aid of a baseflow separation algorithm, and storms were selected by taking the 95% quantile of precipitation. In this case, peak lag and recession lag times were taken as the time between the water table rising by 0.1 cm to a peak and the time taken for it to recede to the same level after the rainfall event. Minimum, maximum, and mean monthly values were plotted using ggplot2 and boxplots produced in the same package for the underlying metrics.

Statistical analyses were performed in SPSS (IBM-Corp., 2016), by firstly testing for normality and homogeneity of variance, and where possible parametric ANOVA tests of differences in the mean values of each group were used to test any hypotheses and identify any significant differences between sites and location (Flanders Moss/Forsinain). Where the data deviated from a normal distribution or homogeneity of variance was not satisfied, it was transformed in SPSS, or non-parametric Kruskal-Wallis tests were used. *Post-hoc* tests were used to determine significant differences for parametric tests, and pairwise comparisons were used for the same purposes for non-parametric Kruskal-Wallis tests. Correlations were calculated in SPSS, using Spearman's rank correlation coefficients (r_s), and Mann-Whitney U tests were used for non-parametric analysis of differences between the locations.

4.3 Results

4.3.1 Climate conditions during the study

The total monthly rainfall and mean monthly air temperatures from April 2018 until the end of November 2019 are shown in (Table 4-2) for both locations. In 2018, the annual precipitation was 1001 mm and 742 mm at Flanders Moss and Forsinain, respectively, with the driest spring/summer in 15 years (Met Office *et al.*, 2018). Mean monthly temperatures ranged from 2.7 to 16.6 °C at Flanders Moss and 1.7 to 15.4 °C at Forsinain over the study. The period between April 2018 and August 2018 was unusually warm and dry at both locations, and, in Scotland, the summer of 2018 was the sixth warmest since 1884 (Met Office *et al.*, 2018). At Forsinain, no rain was recorded for 36 consecutive days between 15 June and 21 July 2018.

Table 4-2 – Temperature and rainfall at Flanders Moss (raised bog) and Forsinain (blanket bog) from January 2018 – December 2019, where Temp = temperature (°C) and P = precipitation (mm).

	Flanders Moss				Forsinain			
	Temp (°C)			P (mm)	Temp (°C)			P (mm)
Month/Year	Mean	Min	Max	Total	Mean	Min	Max	Total
Jan-2018	2.9	-7.0	11.7	168	1.8	-8.6	9.2	75
Feb-2018	2.7	-5.5	11.5	32	1.7	-6.2	9.8	39
Mar-2018	3.5	-5.7	11.3	72	2.6	-7.5	11.1	81
Apr-2018	7.9	-2.9	18.9	64	7.1	-5.3	18.6	41
May-2018	12.0	-1.3	25.2	23	11.3	-2.3	24.4	25
Jun-2018	15.0	5.5	31.7	99	13.0	3.3	27.2	13
Jul-2018	16.6	6.7	26.9	38	15.4	5.5	28.2	47
Aug-2018	14.2	3.9	22.8	72	13.1	2.8	23.3	47
Sep-2018	11.7	1.4	20.1	93	10.5	2.7	24.8	138
Oct-2018	9.1	-3.6	20.1	94	8.0	-4.4	18.8	130
Nov-2018	7.2	-0.7	14.7	154	6.3	-3.3	14.9	53
Dec-2018	4.9	-3.8	12.0	93	4.1	-5.0	12.1	53
2018	**9.0**	**-7.0**	**31.7**	**1001**	**7.9**	**-8.6**	**28.2**	**742**
Jan-2019	3.4	-6.0	11.2	34	2.4	-6.6	10.9	131
Feb-2019	5.9	-7.6	14.9	67	5.6	-6.4	17.3	58
Mar-2019	6.4	-2.9	13.4	147	5.6	-2.7	13.8	107
Apr-2019	8.7	-2.1	23.5	29	8.1	-3.0	21.8	60
May-2019	9.9	-0.6	23.6	65	8.0	-3.6	21.6	98
Jun-2019	13.5	4.1	26.4	52	11.9	3.7	26.0	68
Jul-2019	16.6	6.2	29.6	85	15.0	3.0	27.0	65
Aug-2019	15.6	7.0	27.9	130	13.8	5.3	26.4	154
Sep-2019	12.7	3.2	22.2	72	11.3	1.1	22.7	52
Oct-2019	8.3	-1.7	16.1	104	7.2	-3.6	14.1	65
Nov-2019	4.8	-5.7	12.4	68	3.8	-6.0	9.8	140
2019	**9.7**	**-7.6**	**29.6**	**854**	**8.5**	**-6.6**	**27.0**	**1000**

4.3.2 Water balance

A comparison of the precipitation, discharge and estimated evapotranspiration for the 2018/19 water year is given in Table 4-3a. The annual groundwater storage change varied from 0.2 to 13.6 mm and was lowest at BBR2 and highest at BBAB. Therefore, it was a small component of the water balance, and our AET values can be deemed to be a reasonably reliable estimate. The runoff/rainfall coefficient was the least for their respective locations in the two afforested catchments, which experienced the greatest evapotranspiration losses. Overall, evapotranspiration losses were significantly higher at the raised bog ($p < 0.001$ Mann-Whitney U Test) than at the blanket bog location (412 – 742 versus 212 – 405 mm) and the runoff/rainfall coefficients lower (41.4 – 59.7 versus 64.9 – 80.6%). The runoff/rainfall coefficient was comparable between RBIB and RBR2. However, new dams added to the outflow of BBR2 on 23 March 2019 redirected some of the flow away from the weir. Therefore, the runoff/rainfall coefficient is lower than expected and similar to that at BBAB. We include water balance calculations for the blanket bog sites before (Table 4-3b) and after (Table 4-3c) this event to highlight the impact on the runoff/rainfall ratio.

Table 4-3 (a) – Water balance and mean, maximum and minimum discharge for the eight catchments (1st Oct-18 – 30 Sept-19). (b) - Water balance at the blanket bog before (22/07/18 - 23/03/19) and (c) - after new dams (23/03/2019 - 03/12/2019.). RBAB1 was taken as the afforested catchment for the raised bog. P = precipitation (mm); Q = total annual discharge (mm); Mean Q = mean annual discharge (L s⁻¹)/(mm d⁻¹); Max Q = maximum annual discharge (mm d⁻¹); Min Q = minimum annual discharge (mm d⁻¹); Runoff/rainfall = Q/P (%);AET = actual evapotranspiration P-Q (mm). * - rainfall from the Flanders Moss National Nature Reserve rain gauge.

	Site	P (mm)	Q (mm)	Mean Q (L s⁻¹)	Mean Q (mm d⁻¹)	Max Q (mm d⁻¹)	Min Q (mm d⁻¹)	Runoff/ rainfall (%)	AET (mm)
a	RBIB	1022*	610	1.2	1.7	10.1	0.2	59.7	412
	RBAB1	1267	524	0.1	1.4	16.8	0.0	41.4	742
	RBR1	1267	673	0.5	1.8	16.1	0.0	53.1	593
	RBR2	1267	751	6.3	2.1	87.9	0.0	59.3	516
	BBIB	1093	881	0.5	2.4	35.1	0.0	80.6	212
	BBAB	1093	688	1.1	1.9	35.5	0.0	63.0	405
	BBR1	1093	782	0.4	2.1	35.5	0.0	71.6	311
	BBR2	1093	710	0.5	1.9	31.7	0.0	64.9	383
b	BBIB	778	561	0.4	2.3	23.6	0.0	72.1	217
	BBAB	778	550	1.3	2.3	21.0	0.0	70.7	228
	BBR1	778	549	0.4	2.3	21.4	0.0	70.6	229
	BBR2	778	693	0.7	2.8	31.7	0.0	89.1	85
c	BBIB	762	607	0.5	2.4	35.1	0.0	79.6	156
	BBAB	762	309	0.7	1.2	35.5	0.0	40.6	453
	BBR1	762	459	0.3	1.8	35.5	0.0	60.1	304
	BBR2	762	197	0.2	0.8	9.2	0.0	25.9	565

4.3.3 Seasonal rainfall, runoff and water table

The dry spring/summer of 2018 coincides with a steep drop in the water table at both locations (Figure 4-2). The magnitude of storm peaks was similar except in a period of intense thunderstorms in the summer of 2019 at the raised bog and spring/summer 2019 at the blanket bog location where RBR2 and BBIB experienced higher discharges than the other sites relative to their catchment areas. Some of these peak discharges at RBR2 probably resulted from backing up of the River Forth into the catchment, so they do not necessarily reflect RBR2 stream dynamics. The most intense rainfall events at both locations occurred on 31 August 2019 for the raised bog, which overtopped the weir at RBR2, and 5 August 2019 at the blanket bog, which led to downstream flooding the next day.

The baseflow components over the study period were variable between the different sites. RBIB had the highest baseflow index (BFI = 0.86) at the raised bog, where there was no obvious channelling of water. The BFI at RBAB1 was 0.70, and the restoration catchments had the lowest BFI (RBR1 = 0.65; RBR2 = 0.52;). The BFI at the blanket bog differed, being highest in the two restoration catchments (BBR1 = 0.68; BBR2 = 0.77) and lowest in the forestry (0.64). The BFI for BBIB was 0.66. The flow duration curves at the blanket bog were comparable across the sites, except for the highest 1 % of flows where there was a step-change in discharge in the AB and R1 sites (Figure 4-3). The curves for BBIB and BBR2 were a smooth S-shape characteristic of low-variability flows and attenuated runoff. At the raised bog, the gradient of the flow duration curves was very similar for AB and R1, but IB and R2 were somewhat different in their response. RBIB experienced a very gentle gradient curve indicative of low variability in discharge, whereas the curve steepened for RBR2, showing extreme peaks for the top 1 % of flow conditions in comparison to the other streams. However, the River Forth backing up may account for some of these. The flatter curve at RBIB is characteristic of greater influence from groundwater discharge.
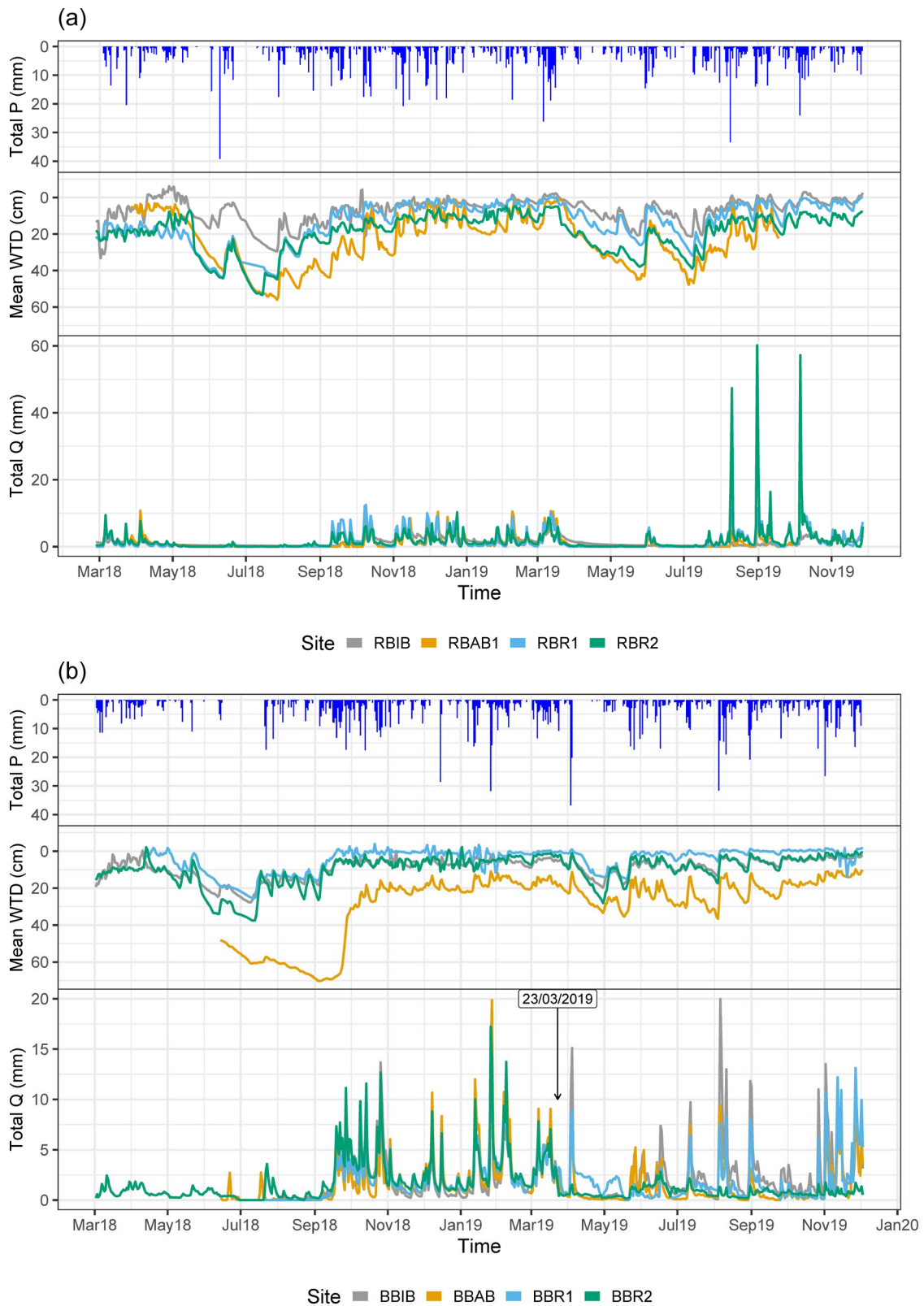
Figure 4-2 – Total daily precipitation (P), mean daily water-table depth (WTD) and total daily discharge (Q) for the catchments at (a) raised bog and (b) blanket bog locations. New dams were added to the outflow of BBR2 on 23 March 2019, as indicated. Note the difference in the y-axis for total Q between the locations. The discharge was similar at both locations except for extreme events at RBR2.
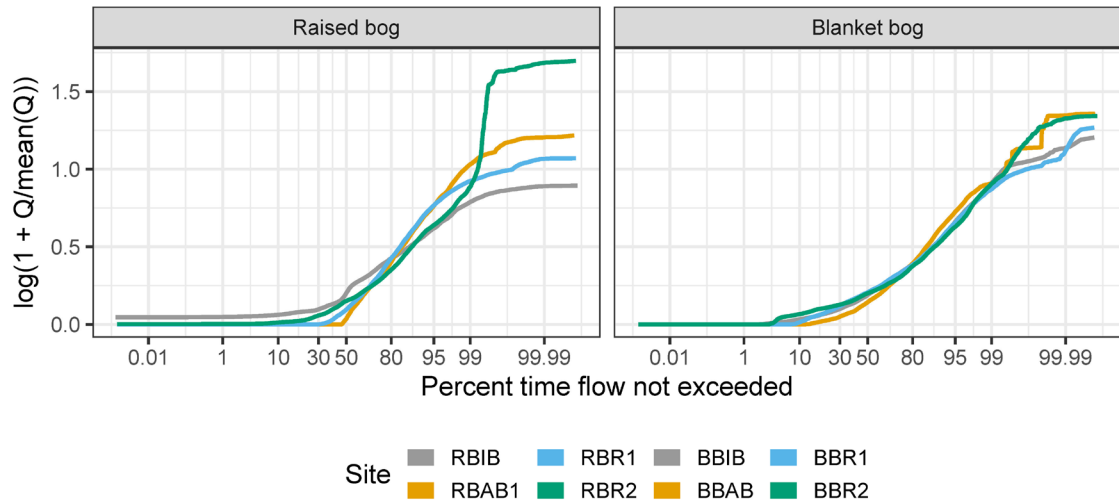
Figure 4-3 – Flow duration curves at 15-minute time steps for the study streams where RB = raised bog, BB = blanket bog, IB = intact bog, AB = afforested bog, R1 = oldest restoration site and R2 = most recent restoration site.

4.3.3.1 Storm response

A summary of the stormflow metrics for the study period is presented as boxplots in Figure 4-4, and the mean values are included in Table A3-2. Areally-weighted peak storm flows (as mm d^{-1} for the whole catchment) were significantly higher ($p < 0.001$ Mann-Whitney U Test) for the blanket bog (mean = 12.09 ± SD 6.53 mm d^{-1}), where the runoff/rainfall coefficients were greater (Table 4-3), than the raised bog (mean = 9.77 ± SD 9.78 mm d^{-1}). At the raised bog, peak flows were significantly higher in the two restoration sites than RBIB ($p < 0.001$ Kruskal-Wallis Test), whereas, at the blanket bog, peak flows were significantly higher at BBIB than at BBR1, BBAB, and BBR2 ($p < 0.05$ Kruskal-Wallis Test). Peak lag times were significantly longer ($p < 0.001$ Mann-Whitney U Test) at the raised bog than at the blanket bog and longest in the AB for each location. Peak lag times were shorter than for the IB in the oldest raised bog restoration site (means: RBIB = 14.94 ± SD 6.13 h, RBR1 = 7.07 ± SD 4.66 h), but not in the oldest blanket bog restoration site (BBIB = 6.48 ± SD 9.06 h, BBR1 = 6.61 ± SD 7.73 h). BBIB, BBR1 and RBR1 had significantly shorter peak lag times ($p < 0.05$ Kruskal-Wallis Test) than the other sites at their location.
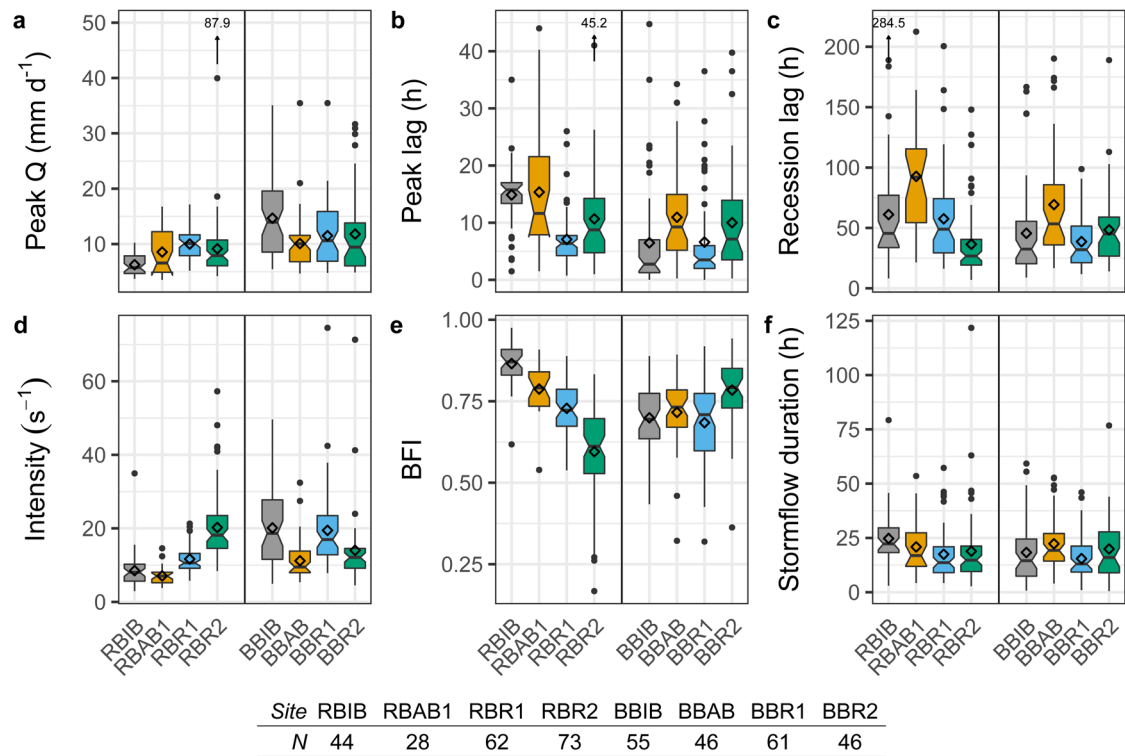
Figure 4-4 – Boxplots of mean stream storm metrics: a) Peak Q (mm d⁻¹); b) Peak lag (h); c) Recession lag (h); d) Hydrograph intensity (s⁻¹) = peak Q/(total Q for storm x 10⁻⁶); e) Baseflow index f) Stormflow duration (h). The diamonds represent means, the notches, and horizontal lines represent medians. The upper and lower limits of the boxes represent the upper and lower quartiles (25%) and the whiskers the variability outside those limits. The points represent any outliers. The number of storms analysed for each site (N) is given in the table.

Recession lag times were significantly higher in the AB ($p <= 0.05$ Kruskal-Wallis Test) at both locations. RBIB, which had the highest baseflow component, had the second-highest recession lag times at the raised bog after the AB. The hydrograph intensity, which indicates the flashiness of the stream response, was highest for RBR2, BBIB and BBR1, with no significant difference between them. The hydrograph intensity was significantly higher for RBR1 than RBIB ($p < 0.001$ Kruskal-Wallis Test), but it was not significantly different between BBR1 and BBIB. The stormflow duration was a measure of how long stormflow persisted and was highest at RBIB (mean = 24.59 ± SD 12.68 h), but there was no significant difference between the raised and blanket bog locations (means: RB = 20.17 ± SD 14.40 h, BB = 18.70 ± SD 12.87 h).

4.3.4 Water-table dynamics

At the raised bog, the water table was at the surface longest at RBIB (10.66%), whereas RBAB1 and RBR2 were never at the surface. However, the peat was fully saturated fractionally longer at RBR1 (0.89%) than at RBAB2 (0.12%). At the blanket bog, the water table at BBAB was never at the surface, but it was at the surface for more time at BBR1 (21.66%) and BBR2 (0.95%) than at BBIB (0.25%). The annual mean water-table depth was similar for RBAB2 (21.3 ± SD 14.8 cm), RBAB1 (23.7 ± SD 14.2 cm) and BBAB (28.7 ± SD 17.1 cm). Water-table depths at the restoration sites were intermediate between the intact and afforested sites except for BBR1, where the water table was at the surface for longer than at any of the other sites (Figure 4-5).
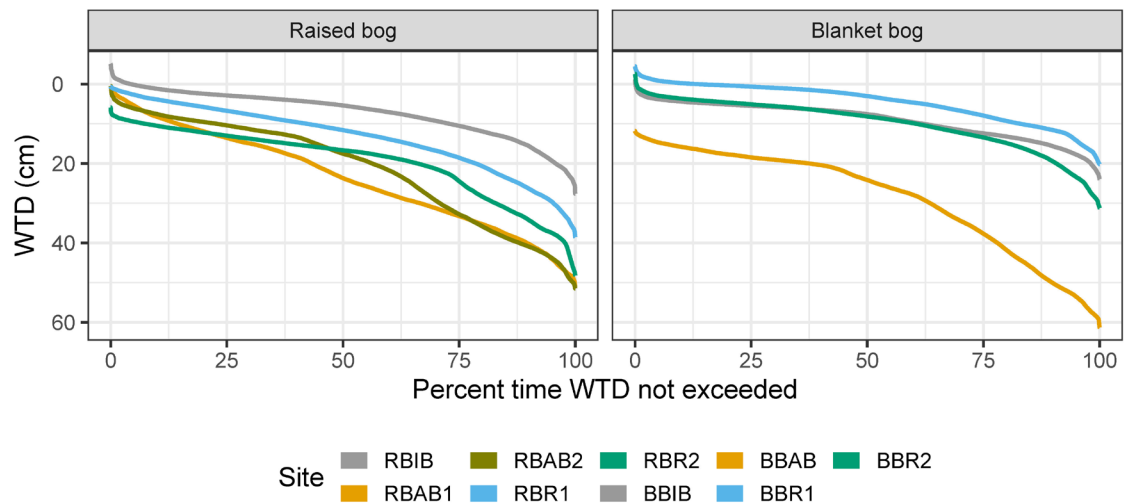
Figure 4-5 – Water-table depth exceedance curves for the raised bog and the blanket bog locations where RB = raised bog, BB = blanket bog, IB = intact bog, AB = afforested bog, RBAB1 = Cardross Moss afforested raised bog, RBAB2 = Flanders Moss afforested raised bog, R1 = oldest restoration site, and R2 = most recent restoration site.

A monthly summary of water-table depth at all sites is presented in Figure 4-6. At the raised bog, the water-table depths at RBR1 were most strongly correlated with those at RBAB2 (r_s = 0.91, p < 0.001, N = 47708), but they were more strongly correlated with RBIB (r_s = 0.067, p < 0.001, N = 59491) than RBAB1 (r_s = 0.65, p < 0.001, N = 49985). The water-table depths at RBR2 were more closely correlated with those at RBAB2 (r_s = 0.89, p < 0.001, N = 47708) and RBAB1 (r_s = 0.79, p < 0.001, N = 51833) than those at RBIB (r_s = 0.65, p < 0.001, N = 49985). However, the water-table depths at BBR1 and BBR2 were more closely correlated with BBIB (BBR1: r_s = 0.76,

$p < 0.001$, $N = 51499$; BBR2: $r_\text{s} = 0.83$, $p < 0.001$, $N = 61483$) than BBAB (BBR1: $r_\text{s} = 0.65$, $p < 0.001$, $N = 51499$; BBR2: $r_\text{s} = 0.79$, $p < 0.001$, $N = 51499$).
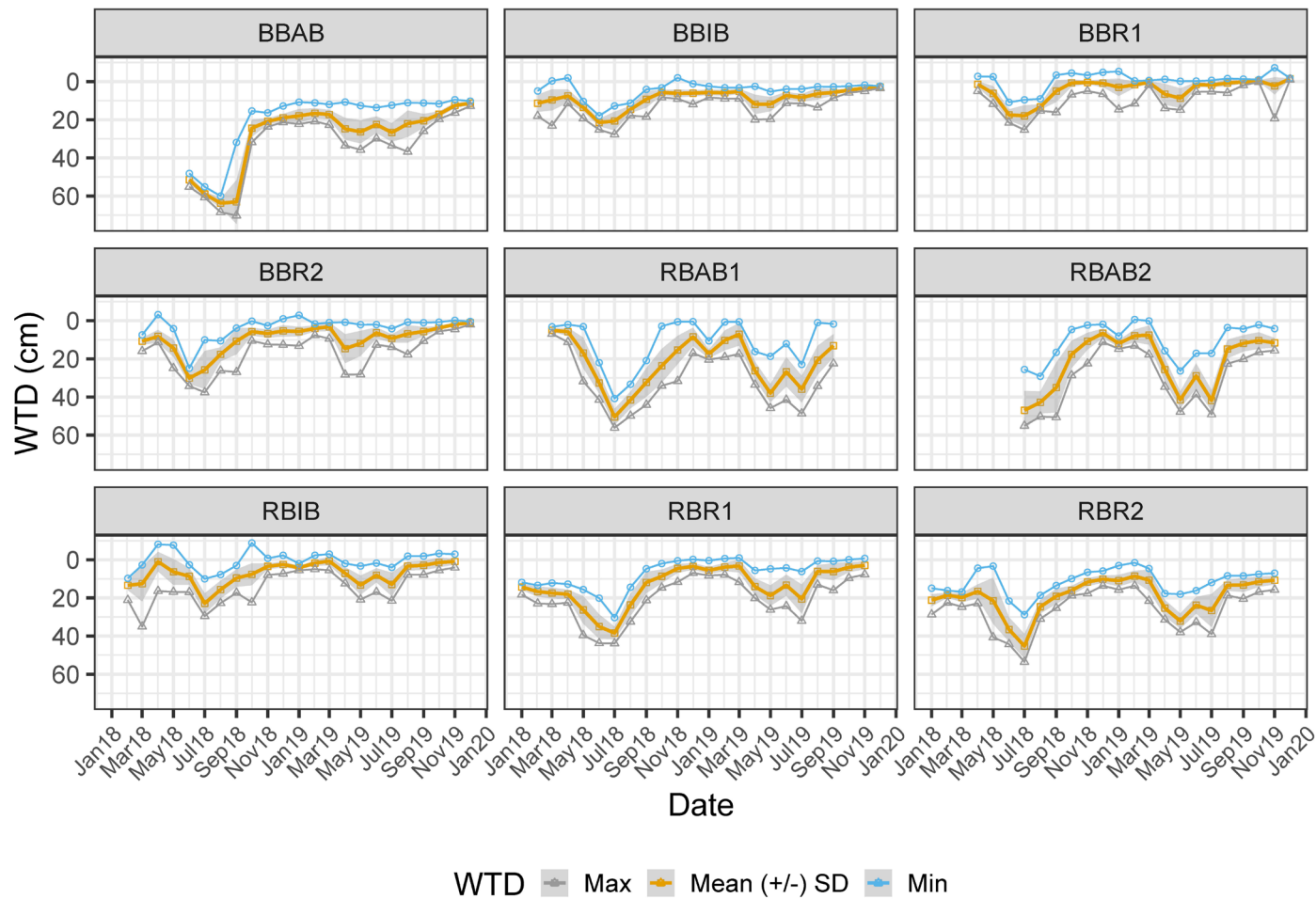
Figure 4-6 – Mean monthly ± SD, maximum and minimum monthly water-table depth (cm) from the instrumented dipwells. The average was taken from two automated dipwells at RBIB and RBR2, whereas the other sites had a single automated dipwell.

The water-table depth also varied between different forestry surface features and natural IB microforms. In the IB sites, the mean water-table depth across both locations was 5.5 cm in hollows ($n = 5$), 8.3 cm in lawns ($n = 3$) and 14.4 cm in hummocks ($n = 5$). In the forestry, the mean water-table depth was 21.1 cm in furrows ($n = 3$), 28.4 cm in ridges ($n = 1$) and 33.2 cm in the original surface ($n = 4$). For the restoration sites, mean water-table depth was 13.3 cm in furrows ($n = 8$), 19.5 cm in ridges ($n = 1$) and 17.7 cm in the original surface ($n = 12$). However, it is important to note that the surface features were not equally balanced, and ridges were underrepresented in this study.

4.3.4.1 Water-table fluctuations

The water table was generally deeper at the raised bog than at the blanket bog sites, except at BBAB (Figure 4-6), and fluctuated more throughout the seasons (Figure 4-2). At the raised bog, seasonal fluctuations were least at RBIB with the annual standard deviation (7.2 cm) less than at the AB (RBAB2 = 14.8 cm; RBAB1 = 14.1 cm) and the two restoration sites (RBR1 = 10.4 cm; RBR2 = 10.9 cm). Seasonal fluctuations in water tables were less in the two blanket bog restoration sites than the raised bog restoration sites, but annual standard deviations followed a similar pattern (BBIB = 5.7 cm; BBAB = 17.1 cm; BBR1 = 6.4 cm; BBR2 = 8.3 cm) except the standard deviation at the IB site was closer to R1 than at the raised bog. The water-table depth deviated away from the IB for the AB and R sites in dry periods at both locations, except BBR2 (Figure 4-2). As the sites began to rewet, the differences between them decreased, but the AB sites took longer to recover. Water-table dynamics at BBR2 and BBIB were remarkably similar throughout the study period except in the summer drought of 2018, where the water-table depth at BBR2 receded beyond that at BBIB. The water table at BBR1 remained shallower than all the other blanket bog sites for most of the study period.

4.3.4.2 Storm response

A summary of the water-table storm metrics is presented in Figure 4-7, and the mean values are provided in Table A3-3. The mean rise in the water table in response to

rainfall events was highest at RBAB1 and BBAB, and overall, it was significantly higher at the raised bog than the blanket bog location ($p < 0.001$ Mann-Whitney U Test). The mean peak water-table depth (when the water table was shallowest during each storm) was deepest in the two afforested sites, RBAB1 and BBAB, and both afforested raised bog sites had significantly lower peaks than at RBIB ($p < 0.001$ Kruskal-Wallis Test). RBR2 also had lower peaks in water tables than RBIB ($p < 0.001$ Kruskal-Wallis Test), yet they were not found to be significantly different between RBR1 and RBIB. There was no significant difference in the peak water table between the blanket and the raised bog, but water tables at BBR1 were significantly shallower than at all other sites ($p < 0.001$ Kruskal-Wallis Test).

The average duration between the commencement of rainfall and a detectable water-table rise was greatest at RBAB1 and BBR1 for the raised bog and blanket bog, respectively. However, there was no significant difference in the time to initial water-table rise between the raised bog and blanket bog locations. RBAB1 and BBAB had the longest water-table peak lag times for their location, and at RBAB1, they were significantly greater than all the other sites at the raised bog ($p < 0.05$ Kruskal-Wallis Test). RBR1 had significantly shorter water-table peak lag times than RBIB ($p = 0.009$ Kruskal-Wallis Test), but they were not found to differ significantly between sites at the blanket bog location. At the raised bog, water-table recession rates were significantly higher at RBAB1 ($p < 0.001$ Kruskal-Wallis Test) than the other sites; however, water-table recession at RBR1 was not significantly different from RBIB. At the blanket bog, recession rates for the afforested and both restoration sites were significantly higher than at BBIB ($p < 0.01$ Kruskal-Wallis Test). The 12-hour recession rate was significantly higher at the raised bog ($p < 0.001$ Mann-Whitney U Test) than the blanket bog, but other than that, no significant difference was found for water-table peak lag times and recession rates between the two locations.
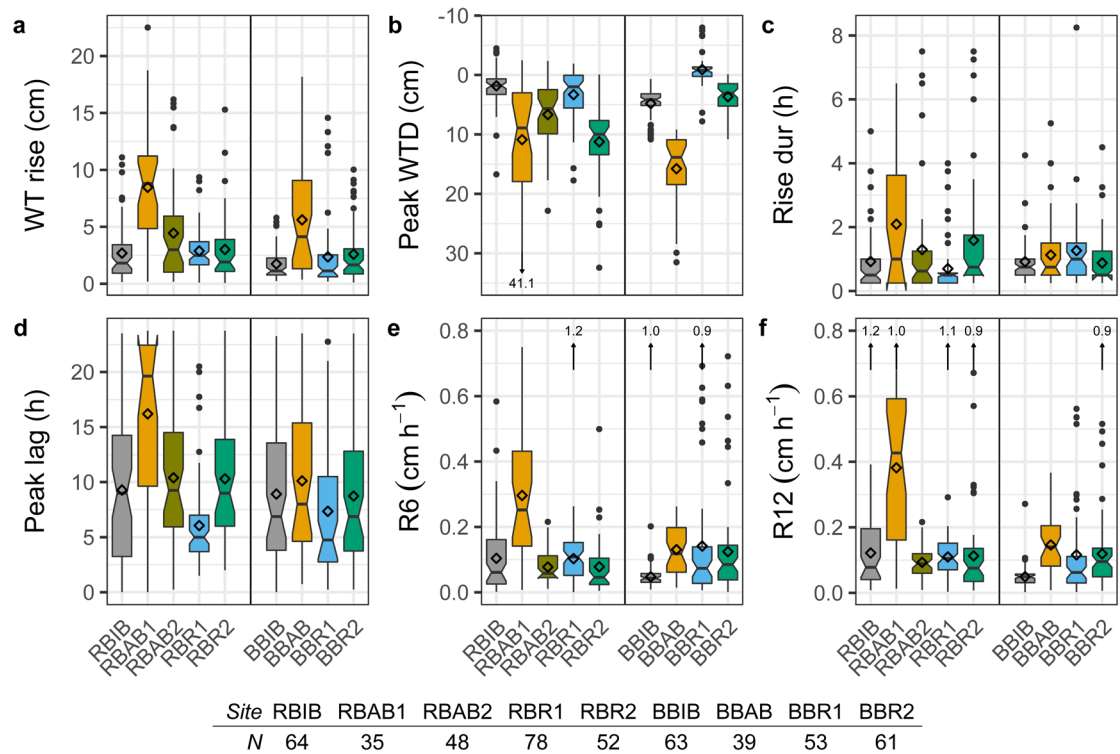
Figure 4-7 – Boxplots of water-table storm metrics: a) water-table rise (cm); b) peak water-table depth (cm); c) time for a rise of 0.1 cm in the water table (h); d) time from rainfall start to peak water-table depth (h); e) 6 hour recession rate (R6) (cm h⁻¹); f) 12 hour recession rate (R12) (cm h⁻¹). The diamonds represent means, the notches, and horizontal lines represent medians. The upper and lower limits of the boxes represent the upper and lower quartiles (25%) and the whiskers the variability outside those limits. The points represent any outliers. The number of storms analysed for each site (N) is given in the table.

4.3.5 Runoff processes

4.3.5.1 Overland flow

Overland flow was detected most frequently at the two IB sites, as expected. When spatially interpolated for the whole catchments, the overland flow frequencies appeared to be associated with elevation (Figure 4-8) and the expected topographic direction of flow in the catchments. Percentage overland flow occurrence between site visits was taken from the average of all crest-stage tubes at each site, where water had collected. At RBIB, overland flow was detected as occurring between 63.9% of site visits compared to 45.8%, 24.6% and 51.0% at RBAB2, RBR2 and RBR1, respectively. At BBIB, overland flow was detected between 86.0% of site visits compared to 29.5%, 73.9% and 61.5% at BBAB, BBR2 and BBR1, respectively. For the IB microforms, overland flow was detected on average for 88.2% of site visits on lawns compared to 68% in hollows and 64.4% in hummocks. Overland flow was detected, on average, across all crest-stage tubes in the forestry, on 41.2% of visits in furrows compared to

36.2% for the other surface features. In the restoration sites, the frequency of overland flow detection was 64.6% and 43.7% for furrows and the remaining features, respectively.
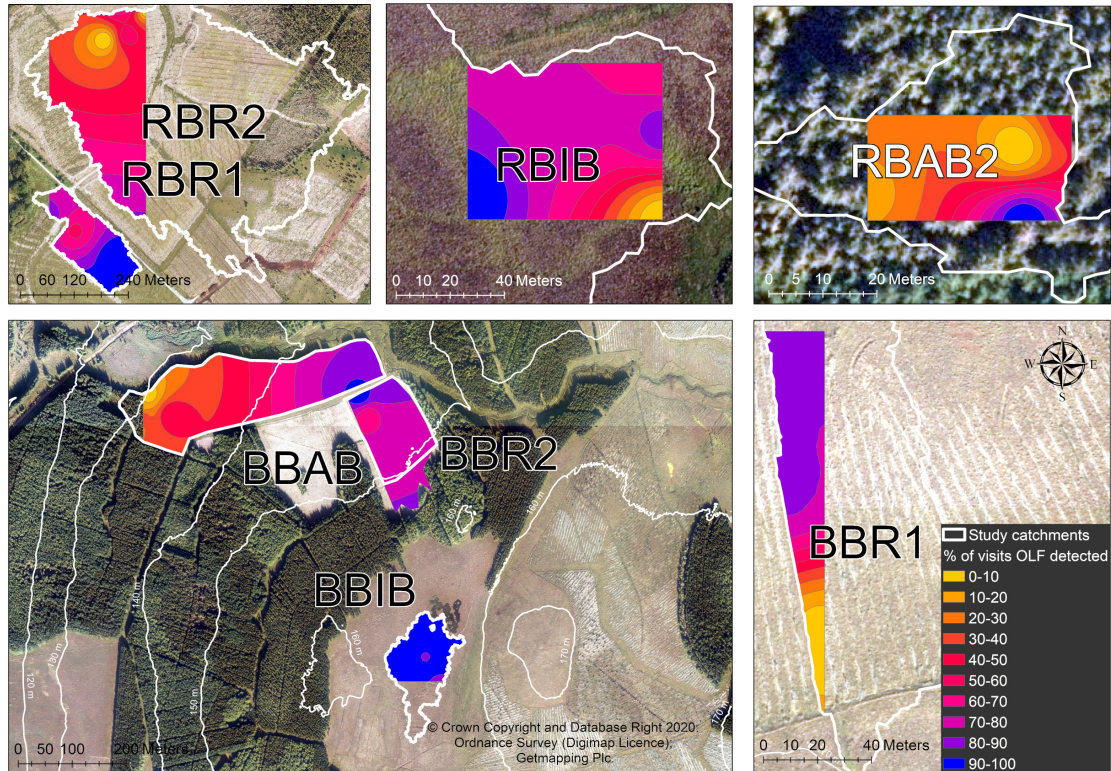
Figure 4-8 – % of visits overland flow was detected interpolated from the crest-stage tubes for the catchments, excluding RBAB1 where there were access restrictions.

TOPMODEL simulations estimated overland flow contributed to 54.6% of total discharge at BBIB and 19.2% for the RBIB. The percentage contribution of overland flow was lowest in the AB (11.9% BB; 2.9% RB) and was greater in the oldest restoration sites (32.2% BB; 8.7% RB), with the raised bog experiencing a higher percentage change. At BBR2, the contribution of overland flow was 15.3%, whereas RBR2 had the highest contribution of overland flow (34.8%) over the whole catchment.

4.4 Discussion

4.4.1 Water balance

For the 2018-19 water year, AET at RBIB was 200 mm greater than BBIB. The mean annual wind speed is ~0.7 m s^{-1} higher at the blanket bog location (Met Office *et al.*, 2018) but could be expected to be cancelled out by lower temperatures and rainfall, leading to similar evaporative demands at both locations. Evapotranspiration losses for RBAB1 and BBAB were 59% and 36% of total annual rainfall, respectively. The difference in evapotranspiration may in part be related to the age and species of tree with lodgepole pine planted in 1965 at RBAB1 and Sitka spruce, planted in 1980 at BBAB. Birkinshaw *et al.* (2014) also showed the importance of the age of Sitka spruce stands in controlling the water balance in the later stages of the Coalburn experiment. Overall, results for the AB are within the range of other studies that reported evapotranspiration losses for conifers to be as much as 55 – 80% of the total annual rainfall in some lowland areas of the UK (Calder *et al.*, 2003; Nisbet, 2005) with lower values (18 - 42%) from some upland studies (Anderson & Pyatt, 1986; Johnson, 1995).

At the restoration sites, AET was lowest in the most recent restoration sites and highest at the oldest restoration sites. Between 22 July 2018 and 23 March 2019, AET at BBR2 (85 mm) was considerably lower than BBIB (217 mm), which could be the result of a layer of mulch on the peat surface intercepting sunlight and preserving soil moisture (Prats *et al.*, 2016) or the relative absence of vegetation. At RBR2, there was still a significant quantity of coarse brash covering the peat surface. AET was ~20% higher than at RBIB, which coincides with reports of 15% interception losses of annual rainfall from conventional felling debris (Anderson *et al.*, 1990; Johnson, 1995; Nisbet, 2005). Water losses can also occur where sufficient understory remains after felling (Nisbet, 2005). However, as is common in coniferous plantations in the UK, little understory was present in the afforested sites in this study, and the vegetation was limited to the less hydrophilic bryophyte species and low diversity of vascular plants (Kershaw *et al.*, 2015). The fact that the oldest restoration sites (RBR1 and BBR1) had higher rates of AET than the IB sites could result from differences in the vegetation at the restoration sites and the near-natural bogs (Hancock *et al.*, 2018). At RBR1, non-characteristic bog plants such as rosebay willowherb (*chamerion angustifolium*) had

established, and at both raised bog restoration sites, conifer seedlings had regenerated naturally. At BBR1, we recorded purple moor-grass (*Molinia caerulea*) when the dipwells were installed, which Hancock *et al.* (2018) used as a negative indication of restoration success, but not from the dipwell locations in BBIB. As hypothesised, the runoff/rainfall coefficient was greatest in the IB, where evapotranspiration losses were least and water tables shallow, and lowest in the two afforested sites where water tables were deeper because of increased evapotranspiration from the trees. The oldest restoration sites had the next lowest water yield. The lower runoff in the oldest restoration sites than the intact sites may be because of more evapotranspiration losses associated with the higher vascular plant density.

4.4.2 Streamflow response and water-table dynamics

At the blanket bog restoration sites, the blocking of drains and furrows could have attenuated runoff and reduced peak flows compared to post-felling and pre-blocking. At the raised bog restoration sites, where ditch blocking had not taken place, peak flows were higher than at the intact site, but the vegetation may also be a key factor. The water-table depth at the raised bog restoration sites was more closely correlated with that at the AB, particularly in drought periods. In contrast, the water table at the blanket bog restoration sites was more closely correlated with that at the IB, suggesting that the inclusion of ditch blocking as part of forest-to-bog restoration supports recovery of the hydrological functioning of bogs. RBAB1 had the lowest hydrograph intensity, which matches the hypothesis that the streamflow response to storms would be more subdued in the AB. Hydrograph intensity and the flow duration curves suggest that RBR1, ~9 years after restoration, exhibited a less flashy regime than RBR2 (despite RBR2's larger catchment size), but not when compared to hydrograph intensity at RBIB.

The higher storm peak lag times at the afforested sites and at the raised bog compared to the blanket bog location coincide with higher water-table rises following storms; the greater water storage capacity would reduce the occurrence of saturation-excess overland flow. Peak lag times for RBR2 were proportionally higher considering the

larger catchment area, but the hydrograph intensity was the highest, and the flow duration curves indicated more extreme peaks for the largest storms than at the other raised bog sites. However, following heavy rainfall, the River Forth often backed up the RBR2 stream, which may explain the contrasting flow duration curve for that site. Shallow subsurface flow dominated at most sites, although 34.8% of flow was found to be overland flow at RBR2, possibly due to steeper slopes on either side of the stream where it flowed through a hollow.

Changes in peat structure due to drying in the tree root zone and ground disturbance may provide new pathways for subsurface flow in afforested and restoration sites. As such, overland flow was detected less frequently from the crest-stage tubes in the afforested and restoration sites when compared to the intact sites, but it was still common. Restoration appeared to reduce baseflows at the raised bog sites compared to the AB, but at the older restoration site (RBR1), BFI appeared to be rising again towards that of the IB. Little difference existed between the blanket bog sites except for BBR2, which had a higher BFI than the other blanket bog sites. The lower BFI in the raised bog restoration sites could be explained by greater compaction from the former tree stands, which were more mature than those at the blanket bog, and interception losses from the brash at RBR2 (Robinson *et al.*, 2003).

There was less difference in the blanket bog catchments sizes than those at the raised bog, and restoration appeared to reduce peak flows at BBR2, which had been restored around 5 years previously. The later addition of new dams by local managers to the outflow of BBR2 reduced average peak flows by a factor of four and resulted in water being redirected away from the weir, thereby changing the catchment area of the weir, causing an apparent reduction in the runoff/rainfall coefficient. BBIB and BBR1 appeared to have the flashiest stormflow response, and BBIB experienced the highest peak flows for its catchment size at both raised and blanket bog locations. BBAB had a more subdued stormflow response than the other blanket bog sites, although the flow duration curve was similar to BBR2. The blanket bog peat was fully saturated for more time in the two restoration sites (where ditch and furrow blocking had occurred) than

the IB. Therefore, depending on the restoration techniques/practices used, water tables can be higher in restoration sites than near-natural sites, as also reported by Menberu *et al.* (2016).

Elevated water tables may benefit the restoration process by facilitating the growth of *Sphagnum spp.*, *Eriophorum spp.* (González et al. 2014) and restricting natural conifer regeneration. Conversely, they may also increase stormflow by reducing the water storage capacity within the peat and increasing the likelihood of saturation-excess overland flow. There can also be an adverse effect of increased methane emissions where the water table is at or very near the surface (Hargreaves & Fowler, 1998). Overall, the hypothesis that storm response would be more subdued in bogs under restoration than intact systems is rejected for the raised bog location, but it was less clear at the blanket bog location given the similarity in the flow duration curves and calculated metrics.

There have been few studies on the effects of ditch blocking on stream and river peak flows (Ballard *et al.*, 2012) and lag times in bog systems despite the widespread belief that it might reduce flood risk downstream (Parry *et al.*, 2014). In this study, there were fewer differences in peak flows between the blanket bog sites, but at the raised bog location, where no ditch blocking had occurred, peak flows were significantly higher in the two restoration sites than for the IB ($p < 0.001$ Kruskal-Wallis Test). Peak flows were lower in RBR1 than RBR2, yet the peak lag time was less at RBR1 than the other catchments at the raised bog. However, it is important to bear in mind that the catchment size of RBR1 was 10 times smaller than RBR2 and three times smaller than RBIB, leading to shorter lag times. Ditch blocking as part of forest-to-bog restoration could be a factor in reducing average peak flows. However, differences in vegetation cover between the restoration sites and the IB may be a more important factor for lag times and hydrograph intensity (Gao *et al.*, 2016; Grayson *et al.*, 2010), particularly where overland flow begins to become strongly dominant during storms. Holden *et al.* (2008) reported that vegetation and surface roughness were important in controlling overland flow velocities in blanket peat. The effects of ditch blocking can also be very

dependent on local conditions (Ballard *et al.*, 2012), and drainage networks have sometimes been found to extend pathways for runoff (Lane & Milledge, 2013).

Water-table fluctuations were least in the IB sites and generally highest in the AB sites. Water tables fluctuated less in the restoration sites than the afforested sites but more than the IB, as shown in other studies (Komulainen *et al.*, 1999; Menberu *et al.*, 2016). Also, the water-table variability was closer to that of the IB in the oldest restoration sites. There were differences between the two locations, with the peak water-table depth being significantly lower than the IB at the raised bog location but not significantly different at the blanket bog location where ditch blocking had occurred. Our hypotheses that we would find deeper and more variable water tables in the AB followed by the restoration sites and that the water tables at the oldest restoration sites would be closer to those at IB are largely accepted. Similarities between the water-table metrics in this study and the ditch blocking study on non-afforested peat by Holden *et al.* (2011) suggest hydrological functioning in forest-to-bog restoration sites is not likely to fully replicate that of near-natural bogs in the short term (<10 years). Our results suggest that ditch and furrow blocking may speed up water-table recovery and attenuate runoff, and mulching may be preferable to conventional felling to preserve soil moisture. However, a more focused study on how the different restoration techniques affect hydrological processes is required.

The peat in the drained, afforested sites was fully saturated for the least amount of time, similar to the findings of Menberu *et al.* (2016), but experienced a higher mean water-table rise during storm events. Overall, there was a negative correlation ($r_s = -0.466$, $p < 0.001$, $N = 360$) between storm precipitation/water-table response ratios and water-table depth at the start of larger storms. Therefore, the greater storage capacity with deeper water tables likely explains the higher water-table rise in the afforested sites. The peat may also have experienced a loss in available pore space after drainage and compression by the trees (Anderson *et al.*, 2000; Anderson & Peace, 2017). Differences in the physical peat properties between the raised bog and blanket bog locations (Chapter 2) could explain the higher water tables in the blanket bog restoration sites. Accelerated water-table recovery may occur where there is less available pore space for the water to fill (Meyer *et al.*, 2011; Rezanezhad *et al.*, 2016),

but this is unlikely because of the similar specific yield between sites (Chapter 2). Overall, the water-table depth after forest-to-bog restoration was similar to that of the IB sites after 5-6 years at the blanket bog location. However, differences still existed in water-table dynamics, and the speed and degree of water-table recovery may depend on restoration methods (i.e. if the drains and furrows were blocked in addition to the felling of trees) and physical characteristics of the peat.

4.5 Conclusions

For the afforested sites, evapotranspiration exerted a dominant control over water yield leading to more subdued streamflow and water-table response to rainfall than for the intact and restored bogs. For sites with no trees, streamflow response to rainfall at the blanket bog restoration sites was more subdued (lower peaks, higher peak lag times) than at the intact blanket bog, whereas at the raised bog restoration sites, streamflow was less subdued than at the intact raised bog. The differences in overland flow occurrence between the intact and the restoration sites were less in the oldest restoration sites than in the most recent restoration sites. Overall, the hypothesis that hydrological functioning would be closest to intact systems in the oldest restoration sites is largely accepted. However, some of the differences between the forest-to-bog restoration sites and the intact bogs we studied suggest a full recovery in hydrological function is not likely to return in the short term (<10 years), although drain and furrow blocking as part of forest-to-bog restoration may provide useful buffering of water tables. An extended time-series study would be required to fully determine whether hydrological functioning changed over long timescales in response to forest-to-bog restoration.

4.6 Acknowledgements

4.7 References

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Chapter 5: The effect of forest clearance for peatland restoration on streamwater quality and fluxes of dissolved organic carbon, nutrients, and potentially toxic elements

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Abstract

We compared streamwater chemistry concentrations and fluxes from the outflows of eight catchments, including two intact, two afforested, and four restored bogs at a raised and blanket bog location in Scotland. The restored sites had been clear-felled 5-17 years earlier, and other post-felling restoration measures had been implemented at the blanket bog location. Dissolved organic carbon (DOC), nutrient and potentially toxic element (PTE) concentrations and fluxes were generally low in the intact bogs and similar between the raised and the blanket bog but significantly higher in the afforested and the recently restored sites. Annual DOC fluxes from the intact sites were 149.8 ± 14.9 kg ha^{-1} yr^{-1} at the raised bog location and 152.3 ± 12.0 kg ha^{-1} yr^{-1} at the blanket bog location. Five years after restoration intervention, annual DOC fluxes were twofold higher at both the raised bog and blanket bog locations than the intact bogs. However, we observed much lower DOC fluxes of 220.8 ± 29.9 kg ha^{-1} yr^{-1} 10 years after forest clearance at the raised bog location and 111.7 ± 16.4 kg ha^{-1} yr^{-1} 17 years after restoration at the blanket bog location. The highest concentrations and fluxes of DOC, phosphate and potentially toxic elements were generally observed in the afforested bogs, but DOC concentrations and fluxes were highest in the youngest blanket bog site that had been mulched. The highest annual fluxes of dissolved

aluminium (1.7 ± 0.001 kg ha^{-1} yr^{-1}) and iron (8.8 ± 0.06 kg ha^{-1} yr^{-1}) were observed in the youngest raised bog restoration site. However, our results suggest a decline in soluble carbon, phosphorus and PTE concentrations and fluxes with time. Although PTEs were higher than intact bog 9 - 10 years post-restoration at the raised bog site, they were similar to intact bog 17 - 18 years post-restoration at the blanket bog location.

5.1 Introduction

Many peatlands have been drained to alter ecosystem conditions for grazing, extraction, gamebirds and agriculture, and some have additionally been afforested for timber and palm oil production (Joosten, 2016). Significant open peatland conversion to forestry has occurred throughout Europe (Andersen *et al.*, 2017), Russia (Strack, 2008), and North America (Chimner *et al.*, 2016). Globally, an estimated 15 million ha of peatlands have been drained for forestry (Paavilainen & Päivänen, 1995; Strack, 2008). More recently, peatlands have been recognised for their wider ecosystem service benefits, such as climate change mitigation through carbon sequestration, nature conservation, and water regulation (Bonn *et al.*, 2016). Therefore, with increasing realisation and interest in peatland ecosystem benefits, schemes to restore afforested peatlands to their former condition through clear-felling and blocking drains have become more widespread. Where the peatlands are ombrotrophic bogs, this has become known as forest-to-bog restoration.

Forest-to-bog restoration aims to restore the hydrological functioning and active peat-forming vegetation. However, there are concerns about the effects of the restoration practices, especially the clear-felling of the trees, on water quality and freshwater ecosystems. Forest-to-bog restoration is not a single practice but involves a combination of methods, depending on the characteristics of the site, such as clear-felling the trees, damming drains and furrows with peat or brash, stump flipping, and mulching (Moffat *et al.*, 2006), all of which commonly involves the use of heavy specialist machinery and equipment (Anderson *et al.*, 2016). These practices can disturb the peat, both physically (Nugent *et al.*, 2003) and biogeochemically (Gaffney

et al., 2018; Howson *et al.*, 2021a; Shah & Nisbet, 2019). Also, tree debris left on the site, within drains or distributed as a mulch across the peat surface, is a major source of soluble carbon and nutrients to soil water (Gaffney, 2017; Gaffney *et al.*, 2018; Howson *et al.*, 2021a) and streams (Muller *et al.*, 2015; Shah & Nisbet, 2019). Thus, forest-to-bog restoration may lead to changes in nutrient and carbon cycling and increased transport to surface waters (Gaffney *et al.*, 2018, 2020; Muller *et al.*, 2015; Shah & Nisbet, 2019), with subsequent impacts on water quality ranging from local effects on water transparency (Shah & Nisbet, 2019), acidity (Gaffney *et al.*, 2018) and metal toxicity (Muller & Tankéré-Muller, 2012) through to downstream effects on aquatic organisms, such as macroinvertebrate assemblages (Drinan *et al.*, 2013a; Ramchunder *et al.*, 2012) and to more sensitive aquatic species such as Atlantic salmon, *Salmo salar*, and freshwater pearl mussel, *Margaritifera margaritifera* (Gaffney *et al.*, 2018; Harriman *et al.*, 1987; Neal *et al.*, 1992; Ormerod *et al.*, 1989; Shah & Nisbet, 2019). Reductions in pH and increase in PTE concentrations such as aluminium (Al) have previously been linked to declines in salmonoid populations (Harriman & Morrison, 1982; Harriman *et al.*, 1987; Rosseland *et al.*, 2007), and the freshwater pearl mussel is particularly sensitive to nitrate and phosphate enrichment (Cosgrove *et al.*, 2017; Strayer, 2014).

There are a limited number of studies that have considered the impact of forest-to-bog restoration on streamwater quality (Gaffney *et al.*, 2018; Muller *et al.*, 2015; Shah & Nisbet, 2019); however, there are many more that have considered the impact of clear-felling on streamwater chemistry (Cummins & Farrell, 2003a, 2003b; Kaila *et al.*, 2014; Rodgers *et al.*, 2010). Brash, remaining on-site, has been attributed to spikes in phosphate (PO_4-P) concentrations in streamwater following felling (Asam, 2012; Asam *et al.*, 2014b; Kaila *et al.*, 2014; Rodgers *et al.*, 2010), the effects of which have been observed to persist from three years (Muller *et al.*, 2015; Shah & Nisbet, 2019) to greater than a decade (Palviainen *et al.*, 2014). Mulched tree debris could lead to greater PO_4-P and soluble carbon losses to streamwater than conventional brash management since it may decompose faster (Moffat *et al.*, 2006). However, few studies have considered how hydrology changes associated with forest-to-bog restoration influence the transport of solutes from their source, through the peat matrix to

watercourses and the resulting chemical fluxes. Fluxes of solutes from forest-to-bog sites may increase due to increased runoff (Howson *et al.*, 2021b; Palviainen *et al.*, 2014) associated with reduced interception from the trees and shallower water tables, increasing the occurrence of overland flow (Holden & Burt, 2003a; Holden & Burt, 2003b). Fluxes are also likely to increase due to changes in carbon and nutrient cycling associated with clear felling. However, it is not clear how the balance of solute fluxes will be driven by changes in stream discharge or on-site production.

After clear-felling, leftover tree debris can be compressed into furrows and drains that provide preferential flow paths into natural streams (Gaffney *et al.*, 2018; Muller *et al.*, 2015; Muller & Tankéré-Muller, 2012; Shah & Nisbet, 2019). Peat disturbances through machine trafficking and other facets of restoration such as stump flipping and peat dam construction combined with well-established legacies of forest acidification (Fowler *et al.*, 1989; Nisbet & Evans, 2014; Nisbet *et al.*, 1995; Ormerod *et al.*, 1989) may also have implications for metal leaching. Muller and Tankéré-Muller (2012) found strong seasonal variations in streamwater potassium (K) and iron (Fe) concentrations and increased leaching of Al and manganese (Mn) to streamwater from clear-felled plots. Asam *et al.* (2014a) found the decomposition of coniferous needles to be a source of nutrients and potentially toxic elements (PTEs) over a two-year incubation period; Al and Fe accumulated in spruce and pine needles, particularly within furrows, whereas Mn and phosphorus (P) were quickly released to the surrounding soil. The fast release of P from brash suggests it may be a significant source for receiving watercourses. Although elevated concentrations of PO_4-P, Fe, and Al have been observed in streams draining clear-felled catchments (Drinan *et al.*, 2013b), other studies have observed little difference in the concentrations of PO_4-P and Al (Gaffney *et al.*, 2018) in streams draining near-natural bog and forest-to-bog sites >17 years after restoration. Shah and Nisbet (2019) observed a dampened increase in streamwater PO_4-P, where phased felling was used in conjunction with low impact harvesting techniques and removal of forest residues.

Currently, we know of only two studies that have quantified chemical fluxes associated with forest-to-bog restoration, and both of those were limited to aquatic carbon (Gaffney *et al.*, 2020; Vinjili, 2012). Gaffney *et al.* (2020) found no significant difference in the annual dissolved organic carbon (DOC) flux between streams draining intact bog and those draining restored catchments shortly after felling, but it should be noted that only a small proportion (12%) of the restoration catchments had been felled. In contrast, Vinjili (2012) reported DOC fluxes from intact bog catchments to be over double those of the afforested catchments and 26% higher than the restored catchments. The two studies used different sub-catchments of the River Dyke in the Scottish Highlands with very similar intact catchment sizes (~70 ha), but the afforested catchment used by Vinjili (2012) was nearly six times larger (900 ha) than that used by Gaffney *et al.* (2020) and the soils and other catchment characteristics may have differed. Vinjili (2012), using method two from Walling and Webb (1985), observed a sixfold higher DOC flux from an intact peat catchment that contained deep peat and peaty podzols than that reported by Gaffney *et al.* (2020), who used method five (Walling and Webb 1985) to estimate the DOC flux. Such differences highlight the difficulty in comparing fluxes between studies where different flux calculations and steam water sampling frequencies have been used. Therefore, there is a need to monitor streamwater quality and determine the flux of carbon and other solutes, such as nutrients and PTEs, using comparable methods from catchments where afforested bog and clear-felled bog are the dominant land use, in order to better understand the impacts of forest-to-bog restoration on water quality and downstream ecosystems.

This study aimed to compare the pH, electrical conductivity (EC) and concentrations and fluxes of DOC, nutrients (total nitrogen, ammonium nitrogen, total phosphorus, and PO_4-P), and PTEs (Al, Fe, and Mn) in streamwater draining intact bog, afforested bog, and forest-to-bog restoration sites at a raised and blanket bog location. The following research questions were addressed:

1. Does streamwater chemistry differ between intact, afforested, and restored sites on raised and blanket bogs?

2. Do streamwater fluxes of carbon, nutrients, and PTEs vary between intact, afforested, and restored sites on raised and blanket bogs?

We hypothesised that streamwater fluxes of DOC and PO_4-P would be highest from the most recently restored sites due to increased streamwater DOC and PO_4-P concentrations being commonly reported following clear-felling. We expected to see the highest EC, lowest pH, and the highest Al, Fe, and Mn concentrations in streamwater draining the afforested sites, given the historic legacy of pollutant scavenging by the trees. We hypothesised that lower concentrations and fluxes of carbon, nutrients and PTEs would be observed in streams draining the oldest restoration sites than the most recent restoration sites but that the streams draining intact bogs would have the lowest concentrations and fluxes of all the treatments.

5.2 Methods

5.2.1 Site descriptions

The two study site locations were Flanders Moss, a series of lowland raised bogs formed over what was once the estuary of the River Forth, and Forsinain in northern Scotland's Flow Country region, the largest continuous area of blanket peatland in Europe (Figure 5-1). The underlying bedrock at Flanders Moss consists of sedimentary sandstones compared to the metamorphic psammites of Forsinain (British Geological Survey, 2020). The average annual precipitation at Flanders Moss was estimated at 1444 mm, and the mean temperature was estimated as 8.7 °C, based on gridded meteorological station interpolations between 1981 and 2010 (Met Office *et al.*, 2018). At Forsinain, the mean annual precipitation was estimated at 1097 mm, and the mean temperature was estimated at 7.4 °C, over the same period. The spring and summer of 2018 were unusually dry and hot, with little rainfall at both locations. An intact, afforested, and two forest-to-bog restoration sites were chosen at each location (Table 1). The intact bog (IB) site at each location was as close to near-natural conditions as we could find. Nearby standing forestry plantations where peat depths exceeded 1 m were used to represent the afforested bog (AB). Two restoration (R) sites were chosen at each location, where standing trees had been felled, and at Forsinain drain and

furrow blocking had also taken place. Drain and furrow blocking had not taken place at Flanders Moss but was scheduled for the future. R1 was the oldest restoration site at each location, although the method and timescale of restoration varied between sites and locations (Table 5-1). It is important to note that identifying suitable afforestation sites that were 100% afforested was difficult due to nearby felling and restoration at both locations. At Flanders Moss, only a small catchment (0.2 ha) was used as osprey nesting (protected species), restricted access to the original instrumented afforested catchment (see Howson et al., 2021b). The catchment's small size resulted in significant flow in the drain, usually only occurring during storms. At Forsinain, the afforested catchment was larger (5.1 ha), but active felling and drain blocking operations were often nearby. More detailed site descriptions are given in Howson *et al.* (2021a).

Table 5-1 – Site features at Flanders Moss (Raised Bog – RB) and Forsinain (Blanket Bog –BB)

Site	Description	Felling dates	Clear-felling and restoration actions	Furrow spacing (m)	Catchment area (ha)	Outflow location	Planting year
RBIB	Flanders Moss intact bog (IB)				6.0	56° 9'47.00"N 4°10'52.29"W	
RBAB	Flanders Moss afforested bog (AB)			1.4	0.2	56° 9'10.12"N 4°20'1.54"W	~1965
RBR1	Flanders Moss restoration site 1 (R1)	24/11/2009 - 18/10/2011	Part conventional harvesting; part low impact harvesting and removal of brash and logs. Re-wetting planned.	1.4	2.5	56° 8'12.88"N 4°19'35.19"W	~1965
RBR2	Flanders Moss restoration site 2 (R2)	01/10/2013 - 31/03/2014	Conventional harvesting (i.e., fell, debranch, extract timber, leave brash). Phased-felling; re-wetting planned.	1.4	26.2	56° 8'27.24"N 4°19'19.27"W	~1965
BBIB	Forsinain intact bog (IB)				1.6	58°25'10.32"N 3°51'41.01"W	
BBAB	Forsinain afforested bog (AB)			1.9	5.1	58°25'30.85"N 3°52'14.67"W	~1980
BBR1	Forsinain restoration site 1 (R1)	2002-2003	Originally, felled-to-waste – furrows & collector drain blocked with peat dams.	1.4	1.6	58°25'58.49"N 3°51'18.76"W	~1980
BBR2	Forsinain restoration site 2 (R2)	2014-2015	Trees felled and mulched on-site – collector drain blocked.	2.3	2.3	58°25'32.21"N 3°51'44.25"W	~1980
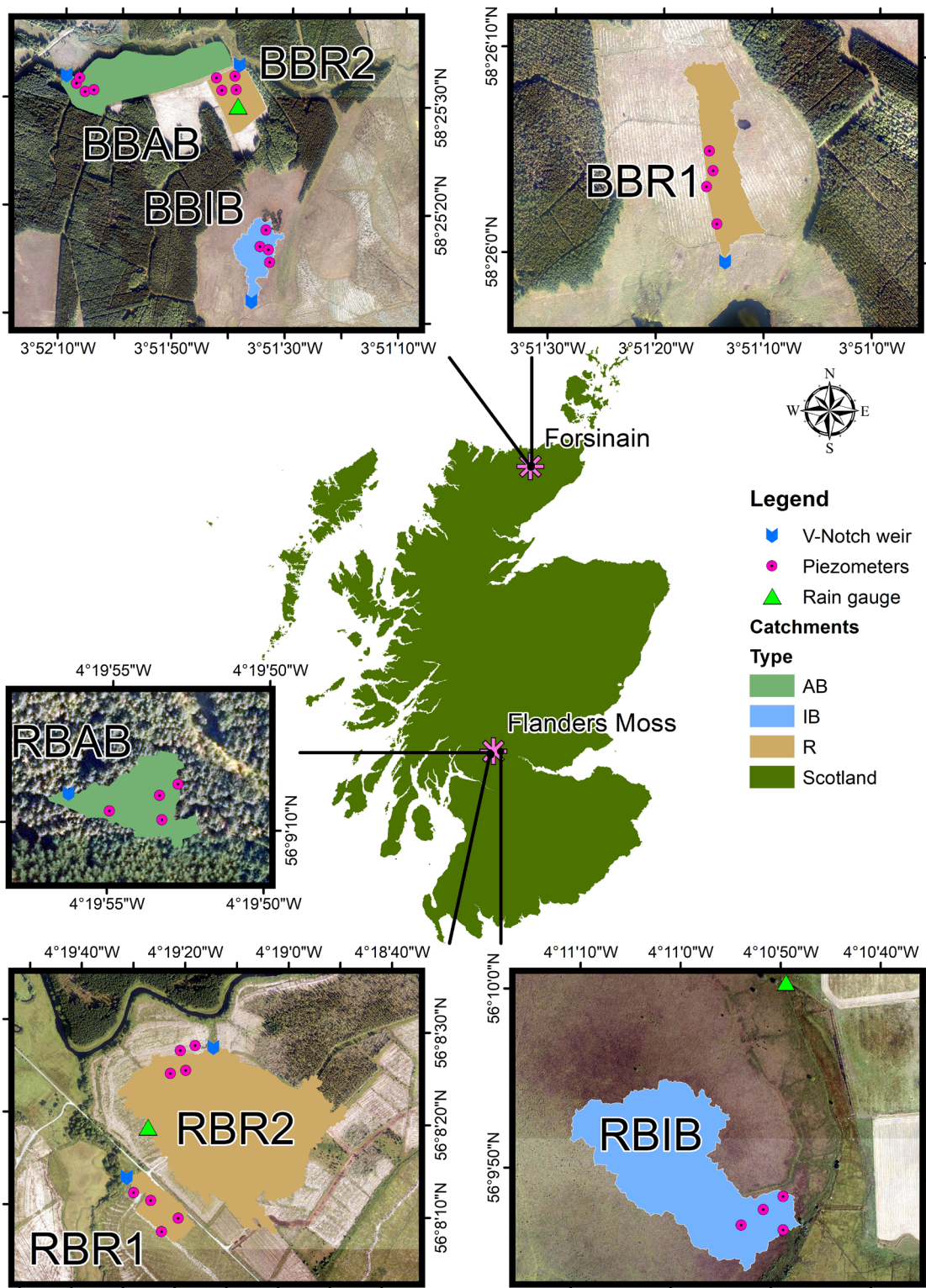
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Figure 5-1 – Experimental design at the raised bog (RB) and blanket bog (BB) location, where IB = intact bog; AB = afforested bog; R1 = oldest restoration site; R2 = most recent restoration site.

The handling of forest debris (brash) was treated differently between the restoration sites. At RBR1, most of the brash was removed. However, remnants of a brash mat still existed in the western part of the catchment 9-10 years after the trees were felled. Brash mats are used in forestry operations to reduce the impacts of machine trafficking on the ground surface. They are usually constructed with an underlying layer of felled tree stems and lesser felled material such as branches and tops overlain to form a relatively smooth surface (Moffat *et al.*, 2006). At RBR2, a significant quantity of tree branches and tops remained on the surface, and in places, they had accumulated in furrows and drains either naturally or as part of the forest clearance. BBR1 was the oldest of the restoration sites (~17 years) and was originally felled-to-waste, which means the trees remained on-site and the brash and tree stems compressed into the furrows and drains. However, the trees were young (~20 years) when they were felled, and little visible brash could be seen during the study period. At BBR2, the trees had been whole-tree mulched, which means the trees were chipped from standing on-site, likely with a mechanical masticator mounted on the arm of an excavator and distributed across the peat surface to leave a smooth layer of wood chips (Moffat *et al.*, 2006). Whole-tree mulching is an alternative to felling, often used where the trees are young or the growth is poor, rendering harvesting uneconomical. New peat dams were also added to the outflow of BBR2 on 23 March 2019.

5.2.2 Monitoring equipment and water sampling

Streamwater samples were taken from the eight hydrologically distinct catchments at monthly intervals between May 2018 and November 2019, except in September 2018, January 2019 and April 2019, when site visits were not possible. At Flanders Moss, the catchment size ranged between 0.2 to 26.2 ha, whereas at Forsinain, they ranged from 1.6 to 5.1 ha (Table 5-1). At the smallest catchment, RBAB, the stream was not always flowing, particularly in the dry spring of 2018 and dry summer of 2019, which meant that only 12 samples of streamwater were collected from this site throughout the study in comparison to 14 from the other sites. At RBR1, the stream flowed through a PVC culvert under a forest track 50 m upstream from the point of sampling.

Streamwater samples were taken from the crests of V-notch weirs, used to monitor discharge at the catchment outflows, except at RBIB, where there was no weir due to the absence of a well-defined channel. Discharge at RBIB was calculated from the hydraulic gradient, and the peat permeability was determined using piezometers (Figure 5-1), as discussed in Howson *et al.* (2021b). At RBIB, water samples were taken where water flow was observed on the bog's perimeter. At each catchment outlet, the following water samples were collected in polyethene bottles: 1L for pH, electrical conductivity (EC), and dissolved nutrients; 500 mL for low-level pH, EC, and total nitrogen and 500 mL for dissolved organic carbon (DOC), and total phosphorus; 50 mL for dissolved metals and 50 mL for total metals. All bottles were pre-rinsed three times before taking a sample and filled to the top to ensure no headspace was present. The samples were packed in an insulated box and refrigerated for transport to the Scottish Environment Protection Agency (SEPA) laboratories within 24 hours, where they were analysed. Additional grab samples were taken in 50 mL centrifuge tubes between April and May 2018 before the SEPA survey was fully operational and in December 2018 when the SEPA laboratories were closed for the Christmas period. Grab samples were analysed at the University of Leeds laboratories and used together with the regular streamwater samples for streamwater analysis of pH, EC, carbon, and nutrients. Interlab comparisons were made by comparing pH, EC and concentrations of nutrients and DOC between the SEPA and University of Leeds laboratories.

5.2.3 Chemical analysis

Streamwater samples at the SEPA laboratories were analysed for pH, EC, total and dissolved nutrients, DOC, and total and dissolved metals. All dissolved concentrations were determined on water samples that had passed through a 0.45 μm filter membrane. A Mettler Toledo T90 terminal, T90 Dosing Unit, InLab 731 conductivity, and DGi 112-Pro pH electrodes were used to measure pH and EC on unfiltered samples. Ammonium-N (NH_4-N), nitrite-N (NO_2-N), soluble reactive phosphorus (PO_4-P), and total oxidised nitrogen (TON) concentrations were measured by colorimetry (Thermo Scientific Aquakem 600 Prime discrete colorimetric analysers) on filtered samples. Nitrate-N (NO_3-N) was calculated by subtracting NO_2-N from TON. Total nitrogen (TN) was determined by converting all organic and inorganic nitrogen to NO_3-N and

eventually NO_2-N by digesting the sample under UV light using potassium persulfate and sodium tetraborate. The resulting NO_2-N was analysed by colorimetry using a Skalar San TN Analyser. Total phosphorus (TP) was determined by a manual colorimetric method (Perkin Elmer Lambda 25 Spectrophotometer) by first converting all phosphorus forms to PO_4-P through persulfate digestion. The detection limits for nutrients were 0.024, 0.148, 0.008, 0.007 mg L^{-1} for NH_4-N, TON, PO_4-P, and NO_2-N, respectively. Below detection limit values were replaced by the detection limit divided by two. DOC samples were passed through a 0.45 µm filter membrane before inorganic carbon was removed using acidification and gas sparging. DOC was then determined by combustion (Skalar Formacs^{HT} TOC analyser), converting all organic carbon to CO_2. Total and dissolved metals (Fe, Al, Mn) were analysed by inductively coupled plasma-optical emission spectrophotometry (Perkin Elmer Optima 7300 DV), where dissolved concentrations were filtered through a 0.45 µm membrane, and total concentrations were unfiltered. The methods for nutrients, DOC and metals are covered in more detail in Appendix A4.

All additional grab samples were first analysed for pH and conductivity using a HANNA 9124 pH meter and HORIBA B-173 EC meter on return to the University of Leeds laboratories. They were then vacuum filtered through 0.45 µm cellulose acetate filters, usually within 48 hrs, then analysed for nutrients using colorimetry (Skalar San++ colorimetric auto-analyser) and DOC by combustion (Analytik Jena Multi N/C 2100C combustion analyser). Filtered blanks were used every 20 samples by passing deionised water through the cellulose acetate filters and subtracting the blank concentrations from the sample concentrations. The auto-analyser measured dissolved ammonium (NH_4-N), soluble reactive phosphate (PO_4-P), total oxidised nitrogen (TON) and nitrite-N (NO_2-N). Nitrate-N (NO_3-N) concentrations were determined by subtracting NO_2-N from TON. The methods for DOC and nutrient analyses are covered in more detail in Appendix A2.

The detection limits for nutrients were 0.01, 0.16, 0.005, 0.002 mg L^{-1} for NH_4-N, TON, PO_4-P and NO_{2}-N, respectively, and values below these were treated as

described above. Over 86% of NO₃-N concentrations were below the detection limits of 0.16 mg L^{-1} for the grab samples and 0.148 mg L^{-1} for the regular streamwater samples analysed by SEPA. NO₂-N was also below the detection limits of 0.007 mg L^{-1} for over 61% of streamwater samples; therefore, NO₃-N and NO₂-N concentrations are not presented.

5.2.4 Flux calculations

Annual fluxes for the 2018-19 water year and standard errors were calculated for carbon, nutrients, and PTEs using method five from Walling and Webb (1985), based on the mean discharge and the mean discharge weighted concentration. This method of calculating streamwater fluxes is widely used (e.g., Dinsmore et al., 2013; Gaffney et al., 2020). The flux calculation is given by Equation 1:

$$Flux = K \times Q_r \times \frac{\sum_{n}^{i=1}(C_i \times Q_i)}{\sum_{n}^{i=1} Q_i} \qquad (1)$$

where flux is in kg ha^{-1} yr^{-1}; K = unitless conversion factor for time period; Q_r = mean discharge for the study period (L s^{-1}); C_i = seasonal concentration (mg L^{-1}); and Q_i = seasonal discharge (L s^{-1}). Standard errors were calculated by Equation 2

$$SE = F \times \left[\sum (C_i - C_F)^2 \times \frac{Q_i}{Q_n}\right] \times \frac{Q_i^2}{Q_n^2} \qquad (2)$$

where SE = standard error; C_F = flow weighted mean concentration (mg L^{-1}); Q_n = sum of Q_i values; and F = Total annual discharge. The flow weighted mean is given by Equation 3

$$C_F = \frac{\sum(C_i \times t_i \times Q_i)}{\sum(Q_i \times t_i)} \qquad (3)$$

where C_F = flow weighted mean concentration (mg L^{-1}); t_i = time elapsed between samples (s).

5.2.5 Data and statistical analysis

A composite dataset was produced, including all routine and grab streamwater samples. Due to the lack of afforested streamwater samples at the beginning of the study, statistical comparisons between sites were performed from Aug 2018 to Nov 2019. Statistical analyses were performed in SPSS (IBM Corp., 2016), where the normality and homogeneity of variance were tested before choosing whether to use parametric or non-parametric tests. For parametric tests, analysis of variance (ANOVA) and *post-hoc* analyses determined any significant differences between study sites and location. Kruskal-Wallis tests and pairwise comparisons were used where data deviated from a normal distribution or homogeneity of variance was not satisfied. The effect size (r) was calculated from the Z statistic divided by the square root of the sample size (N), further indicating the magnitude of significant differences (Kassambara, 2020b). Boxplots of the streamwater concentrations of the main measured variables using ggplot (Wickham, 2016) were produced for the eight sites in RStudio (RStudio-Team, 2016). The boxplots were annotated with the significant differences between the afforested and intact sites and between the two oldest restoration sites and the intact sites using individual Mann-Whitney tests (Kassambara, 2020a). Streamwater pH, conductivity, DOC, NO_4-N, and PO_4-P concentrations were compared at the time of sampling at each site. Correlations were calculated using Spearman rank correlation coefficients (r_s). Seasonal changes in the streamwater chemistry for all samples were plotted in ggplot from a sampling time series. Instantaneous flux estimates of DOC, nutrients and PTEs were plotted in ggplot using propagated standard errors from the flux expression and using Rmisc (Hope, 2013).

5.3 Results

5.3.1 Streamwater chemistry

5.3.1.1 Site differences at each location

The pH, EC, DOC, nutrients, and PTEs are presented as boxplots in Figure 5-2, and the medians and significant differences are given in Table 5-2. At Flanders Moss, the highest solute concentrations were observed in the afforested bog, RBAB, except Al was highest at the most recently restored site, RBR2, and Mn was highest at the oldest restored site, RBR1. Kruskal-Wallis tests show the pH of the streamwater was

significantly lower ($p < 0.005$, $r > 0.41$) at RBAB, and EC, DOC, TN, NH_4-N, and PO_4-P significantly higher ($p < 0.01$, $r > 0.30$) than at the other sites. The pH and Mn concentrations were significantly higher ($p < 0.05$, Kruskal-Wallis test, $r > 0.45$) at RBR1 than at any other site. TP concentrations at RBR1 were significantly ($p < 0.05$, $r > 0.30$) lower than at RBAB and, the intact site, RBIB. However, RBIB had the lowest PO_4-P concentrations of the Flanders Moss sites ($p < 0.05$, Kruskal-Wallis test, $r > 0.39$). Dissolved Al concentrations were significantly higher ($p < 0.01$, Kruskal-Wallis test, $r > 0.83$) at RBAB, RBR1 and RBR2 than at RBIB. No significant difference was found between dissolved Fe concentrations at RBAB, RBR1, and RBR2, but all three sites had significantly higher ($p < 0.01$, Kruskal-Wallis test, $r > 0.81$) concentrations than at RBIB.

At Forsinain, the highest concentrations of solutes were observed in the afforested bog, BBAB, except for higher DOC and TN at the most recent restoration site, BBR2. Concentrations of DOC were significantly higher ($p < 0.001$, Kruskal-Wallis test, $r > 0.73$) at both BBAB and BBR2 than at the other sites, with no significant difference between the two. Significant differences ($p < 0.05$, Kruskal-Wallis test, $r > 0.59$) in TP were found between all sites except BBR2 and BBAB, where the concentrations were highest. No significant difference was found in streamwater PO_4-P concentrations between BBR2 and BBAB, but both sites had significantly higher ($p < 0.001$, Kruskal-Wallis test, $r = 0.81$) PO_4-P concentrations than the other Forsinain sites. Mann-Whitney tests identified no significant difference for the streamwater variables presented in Table 5-2 between the intact site, BBIB, and the oldest restoration site, BBR1, except for total and dissolved Mn and TP. However, except for TP and TN, all other measured variables were significantly different between RBIB and RBR1 at Flanders Moss. The streams at Flanders Moss also had significantly higher dissolved Fe concentrations ($p < 0.001$, Mann-Whitney U test, $r = 0.55$) than at Forsinain.

Table 5-2 – Median streamwater concentrations for pH, EC, DOC, nutrients, and PTEs over the study period. EC = electrical conductivity; TN = total nitrogen; TP = total phosphorus. "<0.45 μm" = samples passed through a 0.45 μm membrane (dissolved concentrations). Letters correspond to compact letter displays (CLDs), comparing sites at each location separately. Values for the sites with the same letters are not significantly different at a 0.95 confidence level based on pairwise Wilcoxon rank-sum tests. The highest concentration at each location is highlighted in bold. RB = raised bog; BB = blanket bog; IB = intact bog; AB = afforested bog; R1 = oldest restoration site; R2 = most recent restoration site.

	RBIB	RBAB	RBR1	RBR2	BBIB	BBAB	BBR1	BBR2
pH (pH units)	3.97 [a]	3.68 [b]	**5.43** [c]	4.09 [a]	**4.42** [a]	4.14 [ab]	4.28 [a]	4.07 [b]
EC (μS cm^{-1})	56.30 [a]	**126.00** [b]	44.25 [c]	52.20 [a]	69.50 [a]	**155.50** [b]	72.30 [a]	102.00 [c]
DOC (mg L^{-1})	33.00 [a]	**82.84** [b]	52.81 [c]	54.30 [c]	18.45 [a]	75.10 [b]	21.45 [a]	**85.28** [b]
TN (mg L^{-1})	0.78 [a]	**2.26** [b]	0.76 [a]	1.06 [a]	0.34 [a]	1.31 [b]	0.54 [a]	**1.57** [b]
NH$_4$-N (mg L^{-1})	0.02 [a]	**0.68** [b]	0.13 [c]	0.03 [a]	0.01 [a]	**0.03** [a]	0.01 [a]	0.03 [a]
TP (mg L^{-1})	0.12 [ab]	**0.15** [a]	0.04 [b]	0.08 [a]	0.01 [a]	**0.42** [b]	0.03 [c]	0.30 [b]
PO$_4$-P (mg L^{-1})	0.004 [a]	**0.146** [b]	0.021 [c]	0.048 [d]	0.004 [a]	**0.345** [b]	0.005 [a]	0.224 [c]
Al (μg L^{-1})	78.25 [a]	213.00 [bc]	161.00 [b]	**319.00** [c]	16.90 [a]	**186.00** [b]	21.35 [a]	59.15 [c]
Al <0.45 μm (μg L^{-1})	42.70 [a]	178.00 [bc]	139.50 [b]	**244.00** [c]	12.60 [a]	**161.50** [b]	20.90 [a]	56.60 [c]
Fe (mg L^{-1})	0.40 [a]	**3.09** [b]	1.92 [bc]	1.65 [c]	0.08 [a]	**1.08** [b]	0.12 [a]	0.44 [c]
Fe <0.45 μm (mg L^{-1})	0.25 [a]	**2.77** [b]	1.74 [c]	1.46 [c]	0.07 [a]	**1.06** [b]	0.12 [a]	0.42 [c]
Mn (mg L^{-1})	0.009 [a]	0.011 [a]	**0.100** [b]	0.036 [c]	0.003 [a]	**0.040** [b]	0.012 [c]	0.010 [c]
Mn <0.45 μm (mg L^{-1})	0.007 [a]	0.010 [a]	**0.095** [b]	0.036 [c]	0.003 [a]	**0.040** [b]	0.010 [c]	0.010 [c]
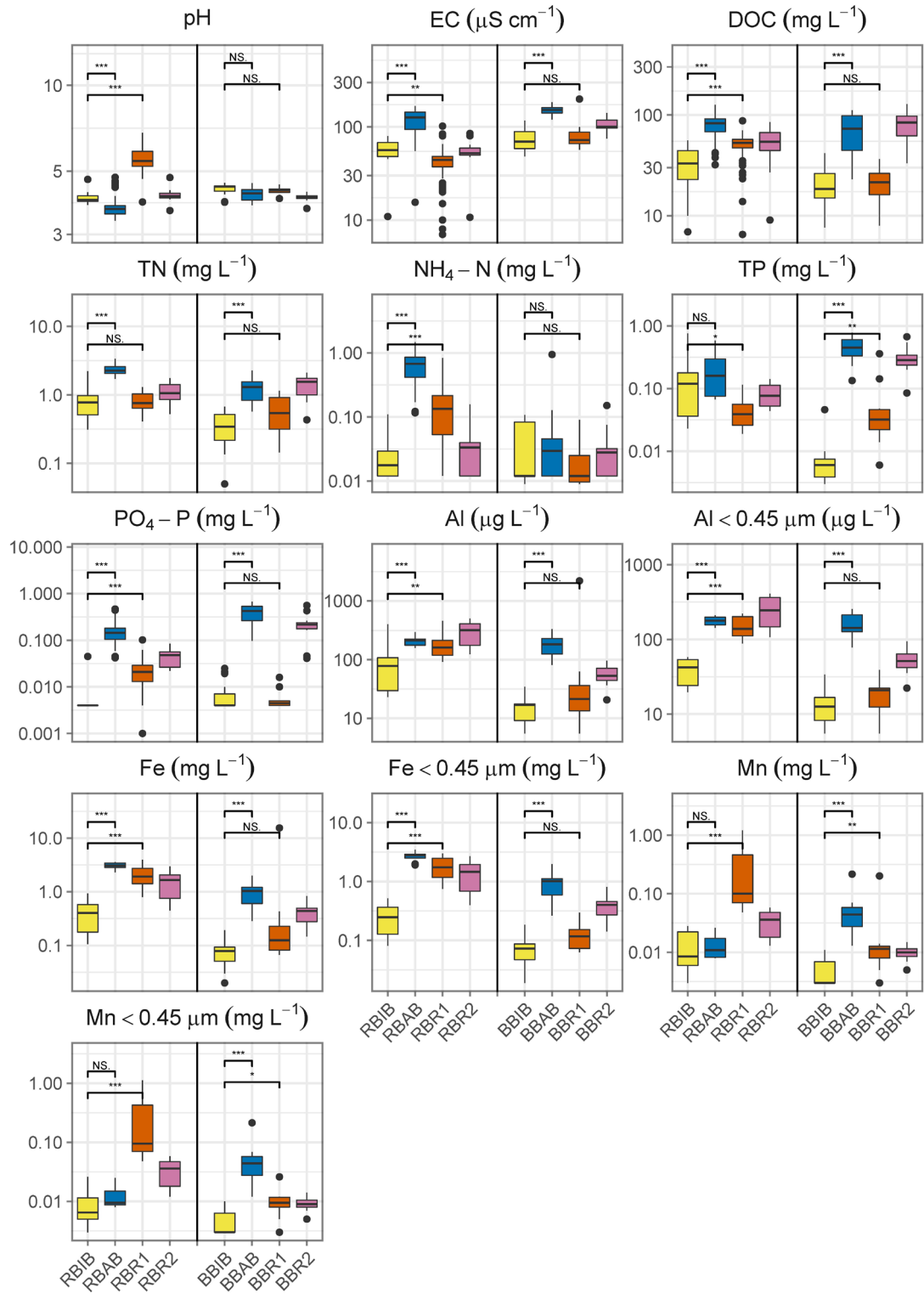
Figure 5-2 – Boxplots of streamwater chemistry for all eight sites (RB = raised bog; BB = blanket bog; IB = intact bog; AB = afforested bog; R1 = oldest restoration site; R2 = most recent restoration site). Significance levels of Mann-Whitney tests between the oldest restoration sites (RBR1 and BBR2) and the intact sites (RBIB and BBIB) and the afforested bog (RBAB and BBAB) and the intact sites are as indicated, where "***" = 0.001, "**" = 0.01, "*"= 0.05, "NS" = insignificant. EC = electrical conductivity; TN = total nitrogen; TP = total phosphorus. "<0.45 μm" = samples passed through a 0.45 μm membrane (dissolved concentrations). Log scales are used to aid readability where there were data outliers. The upper and lower limits of the boxes represent the upper and lower quartiles (25%) and the whiskers the variability outside those limits. The horizontal lines are the median, and the points represent any outliers.

5.3.1.2 Seasonal variability in streamwater chemistry

Seasonal variations in pH and DOC, NH_4-N, PO_4-P, and dissolved Al and Fe concentrations are given in Figure 5-3. At Flanders Moss, streamwater DOC concentrations were similar at the intact and restored sites and followed a similar seasonal pattern, decreasing from high concentrations in late summer 2018 to a minimum in May 2019 before increasing to a peak in August 2019 and then decreasing again into the winter. In contrast, DOC concentrations at RBAB ranged between 50 mg L^{-1} and 126 mg L^{-1} and did not display a strong seasonal pattern. NH_4-N concentrations were generally low for most study sites except RBAB, where concentrations peaked in the summer months. Concentrations of PO_4-P showed a similar seasonal pattern to NH_4-N at RBAB with little seasonality and lower concentrations at the other Flanders Moss sites. Streamwater Al and Fe concentrations followed similar seasonal patterns to DOC, being higher in the late summer and lower in winter, whereas Mn concentrations were low at all sites at Flanders Moss except for a summer spike at RBR1. Stream pH displayed no seasonal pattern, although a small increase was observed in the summer months at the two restoration sites.

At Forsinain, DOC concentrations displayed a strong seasonal cycle at all sites, with the highest concentrations observed in the late summer. However, the seasonal cycle was more pronounced for BBAB and BBR2 than BBIB and BBR1, with peaks of ~ 100 mg L^{-1} observed each year. The seasonality for DOC and PO_4-P was most pronounced at BBAB and BBR2. However, the magnitude of the seasonal cycle for Al and Fe concentrations at BBR2 were more similar to BBIB and BBR1. NH_4-N concentrations were low for most of the year at all Forsinain sites except for a spike observed at BBAB in December 2018. Concentrations of Mn and pH were similar between the different Forsinain sites and displayed little seasonality.
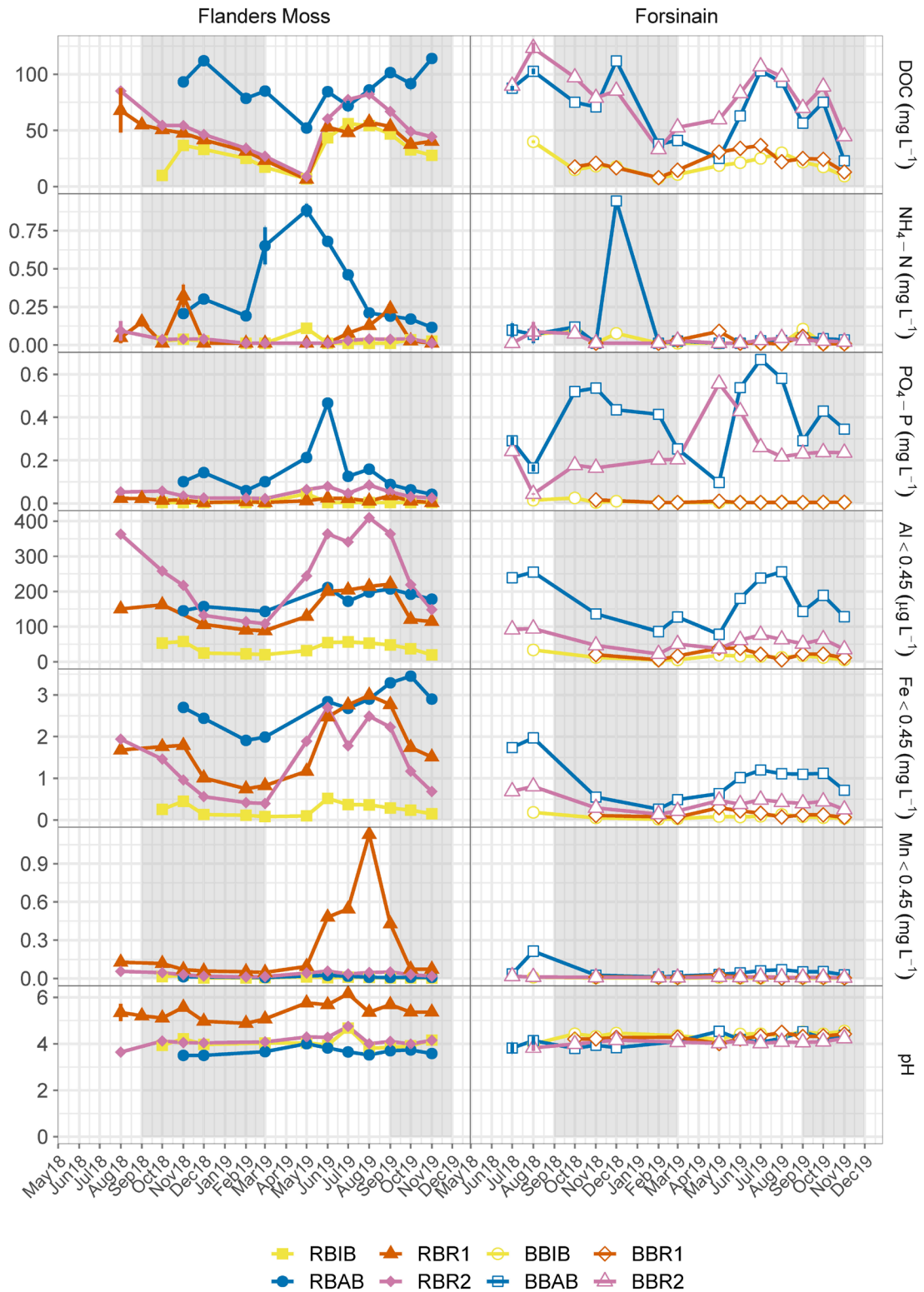
Figure 5-3 – Seasonal variability in streamwater chemistry for DOC, NH₄-N, PO₄-P, dissolved Al, Fe and Mn, and pH for the eight sites (RB = raised bog; BB = blanket bog; IB = intact bog; AB = afforested bog; R1 = oldest restoration site; R2 = most recent restoration site). Shaded areas indicate autumn-winter. Stream samples were not analysed for pH, NH₄-N, PO₄-P, Al, Fe in August 2018 at RBAB. "<0.45" = samples passed through a 0.45 μm membrane (dissolved concentrations).

Dissolved Al and Fe concentrations were strongly correlated with DOC ($r_s > 0.6$, $p <$ 0.05) at all sites, except for Al at RBAB, whereas total Al and Fe were strongly correlated with DOC ($r_s > 0.53$, $p < 0.05$) at all except the intact sites (Figure 5-4). At Flanders Moss, the strongest correlations between Al and DOC were observed at RBR1 and RBR2, and DOC was also strongly correlated with TP and PO$_4$-P at both sites. DOC displayed strong correlations with TN, TP, PO$_4$-P, Al, Fe, Mn, and DOC at RBR1 and RBR2, whereas RBR1 was also correlated with pH (Figure 5-4). At Forsinain, DOC displayed strong correlations with TN, Al and Fe for all sites, but unlike at Flanders Moss, PO$_4$-P did not appear to be associated with DOC. A significant positive correlation existed between DOC and dissolved Mn at BBAB and BBR2. Otherwise, fewer significant correlations were found between metals and DOC at the Forsinain restoration sites. Strong positive correlations between dissolved Fe and PO$_4$-P were observed at RBR1 ($r_s = 0.833$, $p < 0.001$, $N = 13$) and RBR2 ($r_s = 0.917$, $p < 0.001$, $N = 13$), but not at RBIB, RBAB and the less Fe-rich sites at Forsinain.

	RBIB	RBAB	RBR1	RBR2	BBIB	BBAB	BBR1	BBR2
pH	−0.01	−0.15	0.61	0.31	−0.31	−0.51	−0.29	−0.40
TN	0.20	0.54	0.90	0.90	0.92	0.86	0.75	0.65
TP	0.33	0.46	0.84	0.71	0.52	0.56	0.57	0.01
PO$_4$−P	−0.45	0.28	0.75	0.72	−0.14	0.49	−0.14	−0.04
Al	0.35	0.66	0.85	0.84	0.54	0.89	0.76	0.65
Al<0.45	0.60	0.58	0.84	0.86	0.75	0.89	0.76	0.85
Fe	0.68	0.77	0.89	0.76	0.71	0.74	0.74	0.53
Fe<0.45	0.77	0.80	0.84	0.76	0.95	0.75	0.86	0.72
Mn	0.38	0.25	0.87	0.75	0.36	0.67	0.58	0.48
Mn<0.45	0.07	0.07	0.86	0.76	0.39	0.66	0.45	0.60

Figure 5-4 – Spearman rank correlation coefficients between streamwater DOC for the sites (top), pH, nutrients, and metals (left), TP = total phosphorus, TN = total nitrogen. "<0.45" = filtered by 0.45 μm membrane (dissolved concentrations). Blue and red indicate significant positive and negative correlations at the 0.05 confidence interval, respectively. RB = raised bog; BB = blanket bog; IB = intact bog; AB = afforested bog; R1 = oldest restoration site; R2 = most recent restoration site.

5.3.2 Streamwater Fluxes

5.3.2.1 Site differences

Annual streamwater fluxes and their standard errors for carbon, nutrients, and PTEs are presented in Table 5-3. At Forsinain, the highest fluxes for all solutes, except NH_4-N, were observed at BBAB despite having the lowest annual runoff. Although the highest NH_4-N flux was observed at BBR1, there was little difference between sites. Fluxes from Flanders Moss sites did not follow the same pattern due to the much lower annual runoff at RBAB than the other sites (Table 5-3). Therefore, while NH_4-N, TP, and PO_4-P fluxes were highest at RBAB, DOC, TN, Al and Fe fluxes were highest at RBR2, where annual runoff was greatest. Mn fluxes were highest at RBR1, where the highest concentrations were observed. Fluxes of DOC were lowest from the intact site at both locations and similar in magnitude (149.8 kg ha^{-1} yr^{-1} at RBIB and 152.3 kg ha^{-1} yr^{-1} at BBIB). The largest fluxes (approximately double that from the intact sites) were observed from RBR2 and BBAB. At both locations, fluxes of DOC, PO_4-P, and Al were all smaller from the oldest restoration site than the most recently restored sites, and at BBR1 (17 years after felling), the annual export of DOC was 40.6 kg ha^{-1} less than that from BBIB. At Flanders Moss, the DOC flux was 71.0 kg ha^{-1} higher from RBR1 than at RBIB, 10 years after the trees had been felled. However, compared to the afforested sites, annual DOC fluxes were 55.7 kg ha^{-1} and 190.3 kg ha^{-1} less at RBR1 and BBR1, respectively. At both locations, PO_4-P fluxes and flow-weighted mean concentrations were highest from the afforested site and lowest from the intact sites. The PO_4-P flux was smaller from the older restoration site than the recently restored site at each location, but both RBR1 and BBR1 had higher PO_4-P fluxes than RBIB and BBIB, respectively. Streamwater fluxes of total and dissolved Al were lowest from the intact bog site at each location. At Forsinain, the total and dissolved Al fluxes were largest from the afforested bog site, whereas, at Flanders Moss, they were largest from RBR2, the most recently restored site. Fluxes of Al from BBR1 were comparable to those from BBIB, but at RBR1, they were over twice those from RBIB.

Table 5-3 – Annual fluxes for DOC, nutrients, and total and dissolved PTEs (Al, Fe, Mn) for the 2018-19 water year. Annual discharge (mm), the flow weighted mean and annual fluxes (kg ha^{-1} yr^{-1}) are given ± SE for each solute at the eight sites. "< 0.45 μm" = samples passed through a 0.45 μm membrane (dissolved concentrations). The highest values are highlighted at each location. RB = raised bog; BB = blanket bog; IB = intact bog; AB = afforested bog; R1 = oldest restoration site; R2 = most recent restoration site.

	RBIB	RBAB	RBR1	RBR2	BBIB	BBAB	BBR1	BBR2
Annual Q (mm)	610	367	674	**752**	**828**	699	783	711
DOC (mg L^{-1})	27.2 ± 1.6	**96.0 ± 2.7**	39.1 ± 2.4	57.5 ± 2.2	19.0 ± 1.4	**51.9 ± 5.3**	15.4 ± 1.6	51.3 ± 5.4
DOC flux (kg ha^{-1} yr^{-1})	149.8 ± 14.9	276.5 ± 20.8	220.8 ± 29.9	**376.5 ± 36.5**	152.3 ± 12.0	**308.0 ± 158.6**	111.7 ± 16.4	278.0 ± 164.9
TN (mg L^{-1})	0.61 ± 0.05	**2.03 ± 0.05**	0.66 ± 0.04	1.10 ± 0.04	0.38 ± 0.04	**0.93 ± 0.12**	0.34 ± 0.04	0.77 ± 0.11
TN flux (kg ha^{-1} yr^{-1})	3.36 ± 0.01	5.86 ± 0.01	3.75 ± 0.01	**7.23 ± 0.01**	3.15 ± 0.01	**5.48 ± 0.08**	2.44 ± 0.01	4.16 ± 0.07
NH$_4$ (mg L^{-1})	0.02 ± 0.002	**0.22 ± 0.02**	0.02 ± 0.002	0.03 ± 0.001	0.01 ± 0.00	0.01 ± 0.001	**0.02 ± 0.002**	0.01 ± 0.002
NH4 flux (g ha^{-1} yr^{-1})	135.63 ± 0.04	**637.69 ± 0.74**	93.14 ± 0.03	203.11 ± 0.01	93.73 ± 0.0002	85.96 ± 0.01	**118.08 ± 0.02**	78.52 ± 0.01
TP (μg L^{-1})	86.00 ± 18.22	**201.23 ± 22.88**	38.33 ± 3.69	81.64 ± 3.74	10.76 ± 2.34	**509.20 ± 27.20**	29.26 ± 5.94	249.24 ± 20.46
TP flux (g ha^{-1} yr^{-1})	467.73 ± 2.02	**574.36 ± 1.54**	201.83 ± 0.07	535.13 ± 0.11	91.76 ± 0.03	**3050.97 ± 4.14**	213.73 ± 0.22	1364.34 ± 2.38
PO$_4$ (μg L^{-1})	5.32 ± 0.94	**101.47 ± 10.72**	9.55 ± 1.22	42.07 ± 2.14	4.11 ± 0.06	**460.86 ± 22.35**	6.36 ± 0.88	213.41 ± 14.91
PO$_4$ (g ha^{-1} yr^{-1})	29.03 ± 0.01	**291.45 ± 0.34**	55.00 ± 0.01	275.68 ± 0.03	33.22 ± 0.00002	**2763.90 ± 2.79**	46.61 ± 0.005	1171.52 ± 1.26
Al (μg L^{-1})	60.0 ± 10.0	180.0 ± 4.0	140.0 ± 10.0	**300.0 ± 20.0**	10.0 ± 1.0	**120.0 ± 10.0**	10.0 ± 2.0	30.0 ± 4.0
Al flux (g ha^{-1} yr^{-1})	348.22 ± 0.61	527.61 ± 0.06	771.75 ± 0.86	**1953.67 ± 2.04**	102.01 ± 0.01	**713.87 ± 0.92**	97.09 ± 0.02	182.96 ± 0.09
Al < 0.45 μm (μg L^{-1})	0.04 ± 0.002	0.16 ± 0.003	0.12 ± 0.01	**0.25 ± 0.01**	0.01 ± 0.0008	**0.12 ± 0.01**	0.01 ± 0.002	0.03 ± 0.004
Al < 0.45 μm flux (g ha^{-1} yr^{-1})	192.66 ± 0.03	457.52 ± 0.03	659.70 ± 0.36	**1652.76 ± 1.28**	89.36 ± 0.004	**685.38 ± 0.79**	91.96 ± 0.02	185.53 ± 0.07
Fe (mg L^{-1})	0.30 ± 0.03	**2.72 ± 0.07**	1.43 ± 0.19	1.48 ± 0.10	0.07 ± 0.01	**0.46 ± 0.07**	0.10 ± 0.01	0.22 ± 0.03
Fe flux (kg ha^{-1} yr^{-1})	1.64 ± 0.01	7.86 ± 0.01	7.83 ± 0.20	**9.71 ± 0.07**	0.57 ± 0.0003	**2.71 ± 0.03**	0.75 ± 0.0003	1.21 ± 0.004
Fe < 0.45 μm (mg L^{-1})	0.21 ± 0.02	**2.39 ± 0.07**	1.27 ± 0.15	1.34 ± 0.09	0.07 ± 0.01	**0.44 ± 0.07**	0.09 ± 0.01	0.22 ± 0.02
Fe < 0.45 μm flux (kg ha^{-1} yr^{-1})	1.14 ± 0.002	6.90 ± 0.01	6.93 ± 0.12	**8.79 ± 0.06**	0.54 ± 0.0003	**2.58 ± 0.03**	0.67 ± 0.0003	1.17 ± 0.003
Mn (μg L^{-1})	12.49 ± 1.23	12.27 ± 0.74	**140.91 ± 49.76**	32.67 ± 1.72	4.83 ± 0.46	**21.76 ± 3.70**	10.10 ± 0.48	9.41 ± 0.27
Mn flux (g ha^{-1} yr^{-1})	68.50 ± 0.01	35.24 ± 0.002	**844.28 ± 13.36**	214.20 ± 0.02	37.85 ± 0.001	**128.06 ± 0.08**	75.03 ± 0.001	51.67 ± 0.0004
Mn < 0.45 μm (μg L^{-1})	10.44 ± 1.03	10.86 ± 0.48	**136.12 ± 47.08**	32.06 ± 1.65	4.41 ± 0.35	**20.99 ± 3.82**	9.55 ± 0.44	9.10 ± 0.21
Mn < 0.45 μm flux (g ha^{-1} yr^{-1})	57.36 ± 0.01	31.37 ± 0.0007	**815.57 ± 11.96**	210.11 ± 0.02	35.02 ± 0.0007	**123.35 ± 0.08**	70.83 ± 0.001	50.04 ± 0.0003

5.3.2.2 Seasonal variability in streamwater fluxes

Instantaneous fluxes of DOC, nutrients and PTEs for Flanders Moss are plotted, along with discharge at the time of sampling, in Figure 5-5. Higher fluxes were observed in the winter months of 2018 when discharge was greater, but concentrations were lower. Peaks were also observed in late summer 2019, which coincided with extreme rainfall events. Except for Mn and Fe, the other streamwater fluxes showed similar seasonal patterns to the intact bog at the oldest restoration site, RBR1. However, the most recent restoration site, RBR2, experienced a significant peak in DOC, TN, and Al in November 2019, when the discharge was highest. The lowest fluxes were observed in the summer drought of 2018 and a dry spell in May 2019. A similar seasonal pattern in streamwater fluxes was observed from the sites at Forsinain (Figure 5-6), although solute fluxes were high for much of the year in the afforested bog BBAB and the most recent restoration site, BBR2. There was greater seasonal variability in total phosphorous and PO_4-P fluxes at Forsinain for BBAB and BBR2, but they remained close to zero for most of the time at BBR1 and BBIB.
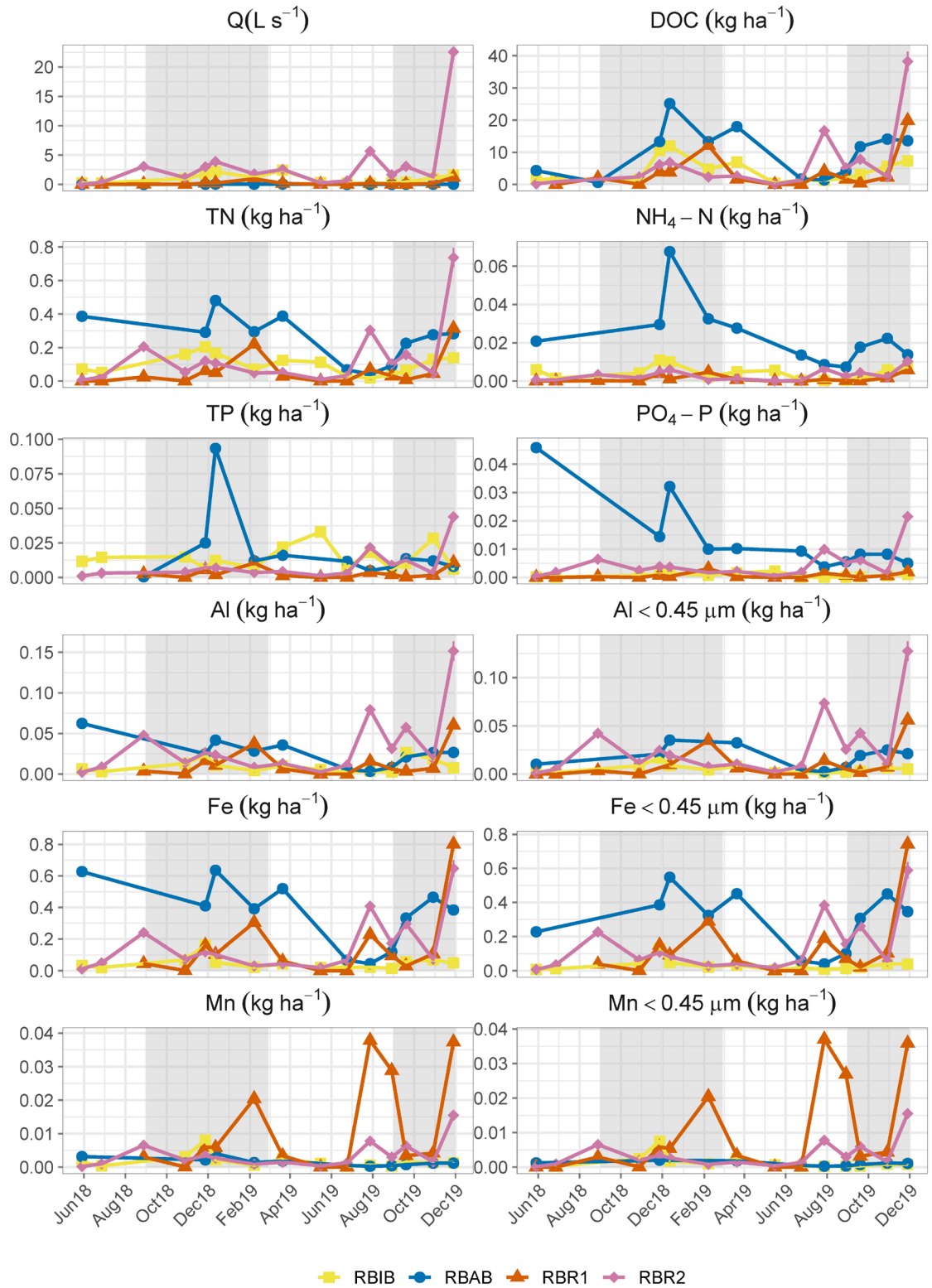
Figure 5-5 – Instantaneous DOC, nutrient and PTE fluxes, and discharge ± SE for Flanders Moss. Autumn and winter are shaded. "< 0.45 μm" = samples passed through a 0.45 μm membrane (dissolved concentrations).
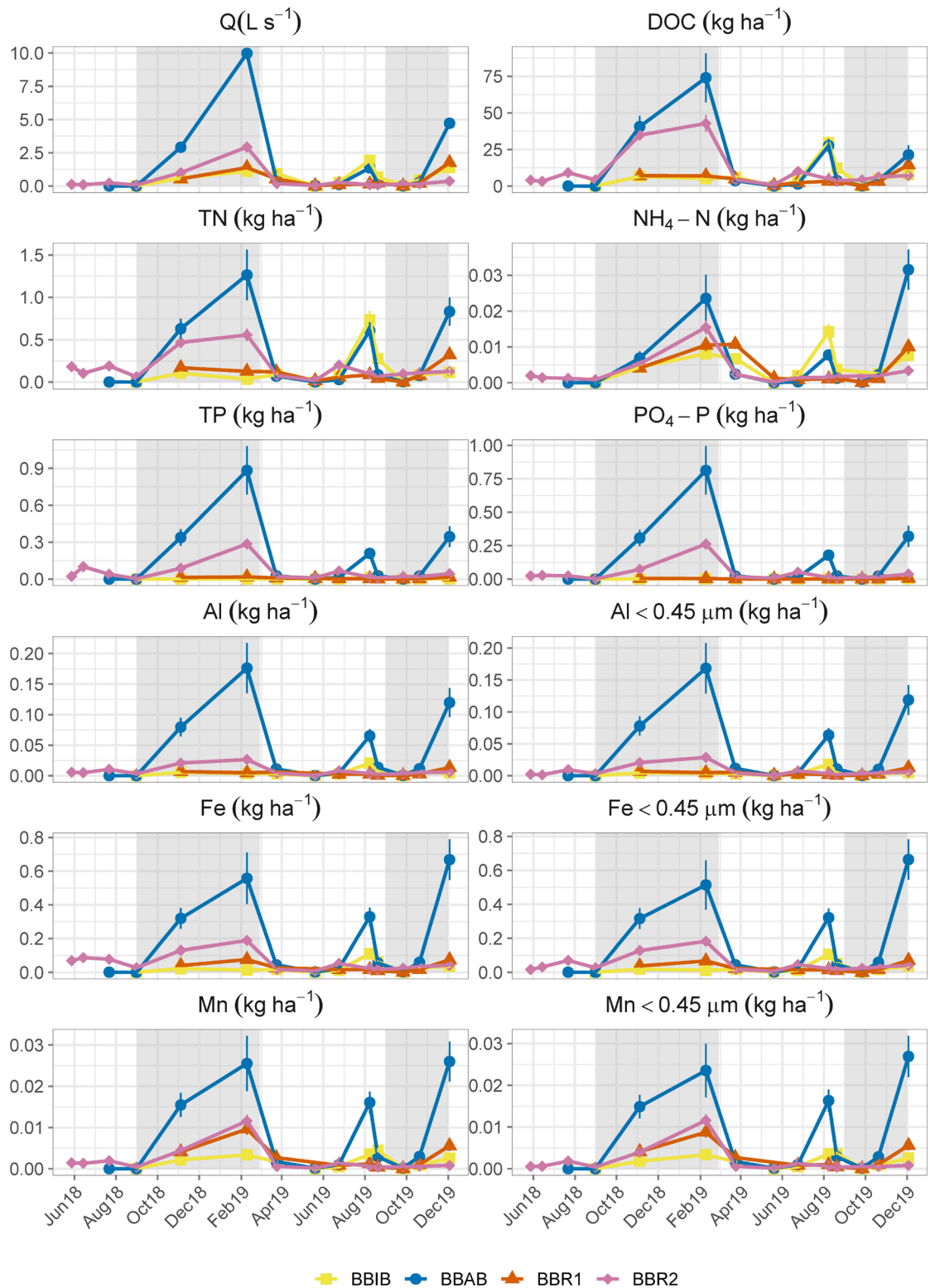
Figure 5-6 – Instantaneous DOC, nutrient and PTE fluxes, and discharge ± SE for Forsinain. Autumn and winter are shaded. "< 0.45 μm" = samples passed through a 0.45 μm membrane (dissolved concentrations).

5.4 Discussion

5.4.1 Streamwater concentrations

5.4.1.1 Differences between sites

At both locations, streamwater solute concentrations were generally lowest in the intact bog and highest in the afforested and the most recent restoration sites, which is similar to the pattern observed in porewater DOC and nutrient concentrations at these sites (Howson *et al.*, 2021a). At Forsinain, the highest EC and concentrations of H^+, TP, PO_4-P, NH_4-N and total and dissolved metals were observed from the afforested bog, BBAB, whereas the highest concentrations of DOC and TN were observed at the most recent restoration site, BBR2, which had been mulched. Streamwater chemistry at the oldest restoration site, BBR1, was very similar to that observed at the intact bog, BBIB, whereas at BBR2, concentrations of H^+, DOC, TN, TP, PO_4-P, Al and Fe were significantly higher than those observed at BBR1 and BBIB. At Flanders Moss, the afforested site also had higher EC and concentrations of H^+, DOC, TN, NH_4-N, TP, PO_4-P and Fe than the other sites. However, Al concentrations were highest at the most recent restoration site, RBR2, whereas pH and Mn concentrations were highest at the oldest restoration site, RBR1. Elevated pH in the RBR1 stream was also detected by Shah and Nisbet (2019), but not in the porewater in the same catchment (Howson *et al.*, 2021a). Shah and Nisbet (2019) suggested several possible reasons for the elevated pH, including base cation inputs from dust due to the proximity to a forest track, although the track was rarely used and mineral horizon inputs from the stream channel may be more likely. The pH at RBR2 was not significantly different from the intact bog, RBIB, and less acidic than RBAB.

Streamflow at RBAB was intermittent and had a very low mean discharge of 38 mL s^{-1} over the study period, compared to the other sites (0.4 – 5.5 L s^{-1}). The low discharge from RBAB may account for the higher concentrations of PO_4-P (mean = 310 µg L^{-1}), DOC (mean = 79.9 mg L^{-1}) and NH_4-N (mean = 0.76 mg L^{-1}) than those reported by Shah and Nisbet (2019) for larger (> 2.5 ha) afforested sites at Flanders Moss, before felling (means: 14-38 µg PO_4-P L^{-1}, 36.6 - 45.2 mg DOC L^{-1}). The intermittent and low flow from the stream at RBAB is likely to lead to the solutes becoming more concentrated in the streamwater, and hence the higher concentrations of individual

solutes stated above and total solutes, as shown by the higher EC for streamwater at RBAB compared to other sites at Flanders Moss (Table 2). However, higher EC and solute concentrations than the intact bog were also found at BBAB, which had much higher discharge, and Gaffney (2017) also observed EC means > 200 µS cm^{-1} from their afforested sites.

DOC and PO$_4$-P concentrations were significantly higher at the blanket bog location in the streamwater draining BBAB and BBR2 than BBIB, but DOC, NH$_4$-N, PO$_4$-P, TN, Al, and Fe concentrations in streamwater at BBR1 were not found to differ significantly from BBIB, 17 years post-restoration. DOC concentrations in the streamwater were highest at BBR2 (Table 5-2) but followed a similar seasonal pattern to BBAB (Figure 5-3). Elevated DOC and PO$_4$-P concentrations at BBR2 were also observed in the site's porewater (Howson *et al.*, 2021a). At BBR2, the finer logging residues (mulch) are likely to be a significant source of soluble carbon (Howson *et al.*, 2021a; Muller *et al.*, 2015) and PO$_4$-P (Asam *et al.*, 2014b; Howson *et al.*, 2021a) to surface waters. However, much of the mulch had already broken down, and the highest concentrations of PO$_4$-P resided in the deeper porewater (Howson *et al.*, 2021a). As such, streamwater PO$_4$-P concentrations were less at BBR2 than BBAB. Gaffney (2017) found that mean PO$_4$-P concentrations in drains were more than 10 times higher shortly after conventional felling, so the impacts of mulching in the early stages of forest-to-bog restoration would likely lead to higher losses of PO$_4$-P and DOC to surface waters than conventional felling and require further study. Other conventional felling studies have also raised concerns about P leaching to surface waters (Asam, 2012; Asam *et al.*, 2014b; Kaila *et al.*, 2014; Koskinen *et al.*, 2011; Koskinen *et al.*, 2017; Rodgers *et al.*, 2010) and O'Driscoll *et al.* (2014) suggested whole-tree harvesting, where most felled debris is removed from the site, should be used as an alternative to conventional felling to protect the biota in streams draining peatland catchments. Shah and Nisbet (2019) observed low impact harvesting and forest material removal for biomass resulted in P concentrations falling from 1.7 mg L^{-1} six months after initial felling to 0.058 mg L^{-1} after four years. These studies highlight the importance of removing as much felled debris as possible and avoiding spreading mulch at forest-to-bog restoration sites that drain into oligotrophic waters and those

that support sensitive protected and priority species such as Atlantic salmon, *Salmo salar*, and the freshwater pearl mussel, *Margaritifera margaritifera.*

At Forsinain, the pH in the streamwater at BBAB was not significantly different from BBIB, despite the shallow porewater being more acidic at BBAB (Howson *et al.*, 2021a). However, at Flanders Moss, the stream pH was significantly lower at RBAB than at the other sites. Higher EC and Na$^+$ and Cl$^-$ concentrations (not shown) in the streamwater draining the afforested sites compared to the other sites at each location is indicative of sea salt scavenging (Dunford *et al.*, 2012; Monteith *et al.*, 2007) by the trees, particularly at Forsinain, which is closer to the coast than Flanders Moss. However, streamwater EC was not significantly different from that at the intact sites in the oldest restoration sites at both locations. Therefore, as Gaffney et al. (2018) observed, the impact of forestry on streamwater chemistry may decline with time after clear-felling. Both acidity and total solutes, as indicated by EC, are significantly lower in the oldest restoration sites than the afforested sites.

Concentrations of Al were significantly higher in the streamwater at BBAB than the other Forsinain sites, suggesting that tree removal on blanket peat is likely to reduce streamwater Al concentrations improving conditions for invertebrates and salmon (Ormerod *et al.*, 1989). However, this was not observed at Flanders Moss, where Al concentrations were highest in the most recent restoration site and over threefold higher than the intact bog in the oldest restoration site. Al and Fe could be linked to disturbance of mineral horizons beneath the peat (Muller *et al.*, 2015; Muller & Tankéré-Muller, 2012) or the decomposition of tree litter (Drinan *et al.*, 2013b; Palviainen *et al.*, 2004). However, the seasonal patterns of Al and Fe concentrations in the recent restoration sites were most similar to those in the intact bog and the older restoration sites suggesting that brash and tree litter are unlikely to be the main source of Al and Fe in our study. Muller and Tankéré-Muller (2012) also found streamwater Al and Fe to be strongly influenced by seasonal cycles and short-term changes in response to rainfall events, probably due to the strong relationship with DOC.

5.4.1.2 Relationships between solutes

The strong positive correlations observed between DOC and Al/Fe may reflect the complexations formed between these metals and humic substances (Boggs *et al.*, 1985; Muller *et al.*, 2015; Muller & Tankéré-Muller, 2012) or the reduction of metal-oxyhydroxides (particularly Fe) through raised water-table levels (Grybos *et al.*, 2009; Nieminen *et al.*, 2015; Nieminen *et al.*, 2017). Furthermore, humic and fulvic acids form ternary complexes with some metals and oxyanions such as phosphate, which Muller and Tankéré-Muller (2012) suggested could increase metal and P mobility from peat to streamwater. Metal-humic substance complexes become more stable with increasing pH (Tipping, 2002; Tipping *et al.*, 2003), possibly explaining the positive correlations between DOC, pH, and Al/Fe/Mn at RBR1, which has the highest pH. Strong positive correlations were observed between DOC and Fe/PO_4-P in the two restoration sites at Flanders Moss which may be due to interactions with ferrous compounds from exposed gley soil horizons in stream channels (PiPujol & Buurman, 1994, 1997). When aerated, mobile Fe (II) ions in gley soils may oxidise to Fe (III), and humic-Fe (III) complexes are known to sequester phosphate under acidic conditions (pH 4 - 5) typically found in bogs (Jones *et al.*, 1988; Koenings, 1976; Shaw *et al.*, 1996). Thus, phosphate sequestration could counteract the effects of eutrophication in streams by reducing P availability. However, the process is reversible with exposure to ambient light (Jones *et al.*, 1988; Shaw *et al.*, 1996); thus, the ultimate fate of P leached from clear-felled sites under the presence of Fe (III) requires further investigation.

5.4.1.3 Environmental impacts

NO_3^- and PO_4^{3-} concentrations below 7.5 mg L^{-1} and 0.06 mg L^{-1}, respectively, have previously been suggested for freshwater pearl mussel survival in rivers, but much lower NO_3^- (0.553 mg L^{-1}) and PO_4^{3-} (0.005 mg L^{-1}) concentrations were thought to be necessary to sustain reproducing populations (Moorkens, 2000, 2006). In laboratory lethal toxicity tests, death of juvenile species occurred at concentrations of between 1000 and 1500 mg L^{-1} for NO_3^-, 5.01 mg L^{-1} for PO_4^{3-} and 954 µg L^{-1} for Al (Belamy, 2020). However, much lower sub-lethal concentrations may still be necessary to sustain a population in the wild, lower than the drinking water threshold of 50 mg L^{-1} for NO_3^-

(EU, 1998) and recommended low alkalinity river PO_4^{3-} concentrations of 0.15 mg L^{-1} (UKTAG, 2013). While NO_3^- concentrations in this study were mostly below the detection limits, median PO_4^{3-} concentrations were over double recommended UKTAG river concentrations of 0.15 mg L^{-1} at the afforested blanket bog site, at Forsinain, and ~50% higher at the most recent blanket bog restoration site, at Forsinain, where the trees had been mulched. Drinking water thresholds for Al, Fe and Mn concentrations are currently 0.2 mg L^{-1}, 0.2 mg L^{-1} and 0.05 mg L^{-1}, respectively (EU, 1998). Median concentrations of dissolved Al exceeded this threshold at the most recent raised bog restoration site at Flanders Moss, and median dissolved Mn concentrations exceeded this threshold at the oldest raised bog restoration site at Flanders Moss. Median dissolved Fe concentrations exceeded the threshold at all but the intact bogs and oldest blanket bog restoration site at Forsinain. Labile Al concentrations exceeding 130 µg L^{-1} may be detrimental for salmon but organically complexed Al is thought to be less toxic to fish (Harriman & Morrison, 1982). Therefore, the binding of metals and PO_4^{3-} to humic substances may reduce the threat to both plants and animals. As the streams in this study were draining peatland, they were enriched in DOC, and the toxicity of Al, Fe and Mn is likely to be reduced. In addition, as the streams in this study were also relatively small, concentrations are likely to be diluted downstream in rivers and not be a cause for concern, but forestry and forestry operations may threaten more sensitive species in headwater streams.

5.4.2 Streamwater fluxes

DOC fluxes were low at the two intact bog locations and similar in magnitude. The highest DOC fluxes were observed at RBR2 and BBAB, although the fluxes at BBR2 will have been underestimated due to new peat dams added to the outflow in the final study year. At Flanders Moss, it is interesting to note that annual DOC flux is approximately 100 kg ha^{-1} higher from RBR2 than RBAB, whereas, at Forsinain, the DOC flux is ~100 kg ha^{-1} lower from BBR2 than BBAB. However, the DOC flux from the oldest restoration site at each location is ~160 kg ha^{-1} lower than from the recent restoration site (Table 5-4). The DOC flux at Flanders Moss was highest at RBR2, where annual runoff was highest, but DOC fluxes were lower than RBAB at RBR1. At Forsinain, the highest DOC flux was observed from BBAB, with similar flux from

BBR2, but ~200 kg ha^{-1} less than BBAB at BBR1. Surprisingly, DOC fluxes were lower from BBR1 than BBIB. Instantaneous flux patterns closely followed instantaneous discharge, but where they did not follow discharge, this was a clear signal that higher solute concentrations controlled the fluxes due to standing and felled trees, particularly at the raised bog location.

A comparison of annual streamwater DOC fluxes from this and other studies is given in Table 5-4. This study used the same flux calculation methods as Gaffney *et al.* (2020) and Dinsmore *et al.* (2010). However, Vinjili (2012) used method two in Walling and Webb (1985) as they sampled streamwater much more frequently. There is also a greater chance that the larger catchments studied by Vinjili (2012) contained a mixture of soil types other than peat (Clark *et al.*, 2007; Gibson *et al.*, 2009) and a greater likelihood of DOC removal with decomposition and adsorption over such large areas, which may have influenced results (Gibson *et al.*, 2009). As in this study, Gaffney *et al.* (2020) and Vinjili (2012) compared DOC fluxes from intact, afforested and recently felled bogs but observed the lowest flux from the afforested bog. Gaffney *et al.* (2020) reported the highest DOC flux from recently felled sites, whereas Vinjili (2012) observed the highest DOC flux from the intact bog. The mean concentrations of DOC in both studies were somewhat lower than those reported in this study for the afforested bogs (Vinjili (2012) = 21.2 mg L^{-1}; Gaffney *et al.* (2020) = 20.3 mg L^{-1}), but mean concentrations of DOC in the intact bogs (Vinjili (2012) = 21.2 mg L^{-1}; Gaffney *et al.* (2020) = 18.3 mg L^{-1}) and the restoration sites (Vinjili (2012) = 47.2 mg L^{-1}; Gaffney *et al.* (2020) = 30.6 mg L^{-1}) were within a similar range to those observed at the blanket bog sites in this study. Average DOC concentrations range between 16.7 mg L^{-1} and 33.4 mg L^{-1} in other non-afforested peatland restoration studies (Wallage, 2007; Wallage *et al.*, 2006; Worrall *et al.*, 2007), perhaps highlighting the influence of forest residues and the smaller catchments on soluble carbon concentrations in this study. We observed DOC concentrations were generally higher at the raised bog location than the blanket bog location with a mean concentration in the intact raised bog of 27.2 mg L^{-1}, slightly higher than the intact blanket bog but lower than the mean concentration of 33.8 mg L^{-1} observed by Dinsmore *et al.* (2010) at Auchencorth Moss, a transitional raised bog.

We observed the lowest annual DOC flux from the oldest blanket bog restoration site where the trees had been felled when they were still young (~20 years), and both drains and furrows were blocked with peat dams. Evidence suggests that DOC concentrations and water colour may increase shortly after ditch blocking, although long-term studies have observed positive effects on DOC concentrations, water colour and resulting DOC fluxes (Wallage, 2007; Wallage *et al.*, 2006; Worrall *et al.*, 2007). Although clear-felling may lead to a short-term increase in DOC fluxes, Palviainen *et al.* (2014) suggested that significant differences in DOC fluxes are not noticeable where felling is limited to less than 30% of a catchment. Hence this may explain why Gaffney *et al.* (2020) did not observe any significant difference in the DOC flux from the intact bog and the recently restored catchment.

Table 5-4 – Annual DOC fluxes (kg C ha^{-1} yr^{-1}) from intact, afforested, and felled and restored sites from a range of studies in Scotland. Means were taken where there were more than one site and year.

	Dinsmore (2010)*	Vinjili (2012)	Gaffney (2020)	This study	
	Raised bog	Blanket bog	Blanket bog	Raised bog	Blanket bog
Intact	254.0 ± 206.0	942.9 ± 59.0	157.1 ± 8.3	149.8 ± 14.9	152.3 ± 12.0
Afforested		403.3 ± 65.0	122.3 ± 4.9	276.5 ± 20.8	308.0 ± 158.6
Restored < 5 years		700.1 ± 107.0	225.9 ± 12.5	376.5 ± 36.5	278.0 ± 164.9
Restored 9 - 10 years				220.8 ± 29.9	
Restored > 17 years					111.7 ± 16.4

* Site had previously had some peat extraction activity.

The PO$_4$-P flux was lowest and of a very similar magnitude from the intact site at both locations (RBIB = 29.03 g P ha^{-1} yr^{-1}; BBIB = 33.22 g P ha^{-1} yr^{-1}). At the blanket bog location, the PO$_4$-P flux was over 70 times higher from BBAB (2763.90 g P ha^{-1} yr^{-1}) and 35 times higher from BBR2 (1364.34 g P ha^{-1} yr^{-1}) than BBIB. There was little difference between the PO$_4$-P flux from the oldest restoration site (RBR1 = 55.00 g P ha^{-1} yr^{-1}; BBR1 = 46.61 g P ha^{-1} yr^{-1}) and the intact bogs. Kaila *et al.* (2014) reported streamwater P fluxes of ~700 g P ha^{-1} yr^{-1} the second year after stem only harvesting of Scots pine at a peatland in south-central Finland, and Rodgers et al. (2010) recorded ~2300 g P ha^{-1} yr^{-1} in the second year after felling in a blanket peatland in Ireland. Kaila *et al.* (2014) attributed the major source of P to the rise in the water table after felling and release from peat, whereas Rodgers *et al.* (2010) attributed it to the release from harvest residues. Harvest residues are the more likely source in this study,

particularly as the highest pore water PO_4-P concentrations were found in locations dominated by brash (Howson et al., 2021a). However, the high TP and PO_4-P fluxes from the forestry sites at both locations suggest similar leaching of P may occur from the tree litter and possible inputs from NPK fertilisers (Cummins & Farrell, 2003b; Kenttämies, 1981). The highest PO_4-P flux at each location occurred at the site with the highest flow weighted mean concentrations: RBAB (101.47 µg L^{-1}) and BBAB (460.86 µg L^{-1}), despite them having the lowest annual runoff. Interestingly, the second-highest TP flux at the raised bog location was observed from RBIB (467.73 g P ha^{-1} yr^{-1}), possibly resulting from the additional organic matter collected in samples where there was no clearly defined stream channel. At Forsinain, the highest TP flux was at BBAB (3050.97 g P ha^{-1} yr^{-1}) and similar in magnitude to the PO_4-P flux, showing that most P is present as inorganic P readily available for uptake by stream flora and fauna.

At Flanders Moss, the highest dissolved Al flux (1652.76 g Al ha^{-1} yr^{-1}) was observed at RBR2, where the flow weighted mean concentration and discharge were highest. At Forsinain, the highest dissolved Al flux (685.38 Al ha^{-1} yr^{-1}), which was almost three times smaller than at Flanders Moss, was observed at BBAB, where the concentrations were highest and the annual discharge lowest. The dissolved Al flux from RBR1 was over threefold higher than that from the intact site (RBIB = 192.66 g Al ha^{-1} yr^{-1}; RBR1 = 659.70 g Al ha^{-1} yr^{-1}), whereas, at Forsinain, there was little difference in the dissolved Al flux from BBIB and BBR1 (BBIB = 89.36 g Al ha^{-1} yr^{-1}; BBR1 = 91.96 g Al ha^{-1} yr^{-1}). Dissolved fluxes of Fe and Mn were similar from BBR1 to BBIB at Forsinain. In contrast, this was not observed at Flanders Moss, where they were 5 and 12 times higher from RBR1 than RBIB for dissolved Fe and Mn, respectively. This result may be a consequence of mineral horizon disturbances after a new spur road had been installed, although RBR1 had been felled 8-9 years later than BBR1. In this study, the release of Al and Fe were more strongly associated with DOC than with pH, and the correlations found with pH were positive, indicating the possible effects of increased pH on metal-humic substance interactions and the solubility of DOC.

Comparisons of instantaneous fluxes at Flanders Moss indicated no significant difference in DOC, total and dissolved Mn fluxes between the different sites. However, significant differences were found between sites for fluxes of all other measured variables. Only the afforested bog was associated with significantly higher fluxes of NH_4-N, which is likely the result of increased ammonification due to deeper water tables and low flow conditions (Daniels *et al.*, 2012). At Forsinain, instantaneous fluxes of PO_4-P and TP were significantly higher in the afforested bog and the most recent restoration site than the intact bog, but there were no other significant differences between sites.

In summary, we accept the hypothesis that the lowest solute concentrations and fluxes were observed at the intact sites. Our hypothesis that the greatest fluxes of DOC and PO_4-P would be associated with the most recent restoration sites was not consistent across locations due to the high concentrations observed in the afforested bogs resulting in the highest fluxes of DOC and PO_4-P being recorded from them. However, the PO_4-P fluxes at BBR2 may have been underestimated after new peat dams were installed near the catchment outlet in the final study year. PTE concentrations and fluxes were not always highest in the afforested bogs, as hypothesised. They were high at RBR2 for Al and Fe and RBR1 for Mn, suggesting restoration can sometimes increase their mobilisation, most likely via complexation with DOC and disturbance of mineral soil beneath the peat. Elevated DOC, Al, Fe and Mn concentrations may have implications for water companies to ensure they are kept below acceptable drinking water guidelines (Khadse *et al.*, 2015; WHO, 2011; Williamson *et al.*, 2020). EC was consistently highest in the afforested bogs, but the acidity was not. Therefore, the hypothesis that we expected to find the streamwater draining the afforested sites to have the highest EC, lowest pH and highest Al, Fe and Mn concentrations is rejected on the basis PTEs and acidity were sometimes higher in the restoration sites. Our hypothesis that carbon, nutrient, and PTE fluxes would be lower from the oldest rather than the most recent restoration sites is largely accepted, except for NH_4-N fluxes, which were highest at the oldest blanket bog restoration site and total and dissolved Mn fluxes, which were higher at the oldest raised bog restoration site.

5.5 Conclusion

DOC, nutrient, and PTE concentrations and fluxes were similar and lowest from the intact raised and blanket bogs. The DOC fluxes for the intact bogs were comparable to other studies in Scotland that had sampled streamwater at monthly intervals. The afforested sites at both locations had the highest NH_4-N, TP, PO_4-P, EC, Fe, and Al concentrations and the highest fluxes of TP and PO_4-P. Annual DOC fluxes were twice as high from the most recent restoration sites (5-6 years after felling) than the intact bogs, but lower fluxes from the oldest restoration sites indicate a potential decline with time. The annual DOC flux from the oldest raised bog restoration site was 76.0 ± 10.81 kg C ha^{-1} yr^{-1} higher than the intact bog 9 - 10 years after felling, but it was 22.66 ± 5.70 kg C ha^{-1} yr^{-1} lower than the intact bog from the oldest blanket bog restoration site 17 - 18 years after felling. Elevated streamwater TP, PO_4-P, and dissolved Al and Fe concentrations five years post-restoration were strongly associated with DOC at the raised bog location but less so at the blanket bog location. Therefore, forest-to-bog restoration can sometimes increase the risk of eutrophication and metal toxicity, and caution should be applied where outflows of restoration sites are into more sensitive oligotrophic waters. Elevated PTE concentrations and fluxes were detected at the raised bog location 9 - 10 years after restoration, indicating more recovery time may be necessary. However, streamwater concentrations and fluxes of carbon, nutrients, and PTEs were at similar levels to intact bogs > 17 years post-restoration at the blanket bog location.

5.6 Acknowledgements

5.7 References

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Chapter 6: Synthesis

6.1 Chapter outline

The planting of commercial coniferous trees on deep peat in the last century has caused significant degradation of raised and blanket bog resources in the UK (Cannell *et al.*, 1993; Hargreaves *et al.*, 2003). Given that peatlands store significant amounts of carbon, the Scottish and UK governments have announced substantial investment and set targets for the restoration and maintenance of peatlands as a part of a wider strategy to mitigate climate change, including the £640 million 'Nature for Climate Fund' for England (Norman, 2020) and a £250 million investment from the Scottish Government for peatland restoration until 2030 (Scottish Government, 2021). Where the peat has been afforested, this restoration is attempted by clear-felling the trees and often by blocking drains and furrows in order to raise the water table to restore peatland functions. Where restoration is on bogs, the process is sometimes termed forest-to-bog restoration. While we know that forest-to-bog restoration has benefits for biodiversity and broader conservation value (Alsila *et al.*, 2021; Laine *et al.*, 1995; Stoneman *et al.*, 2016), we do not fully understand the impact of forest-to-bog restoration on the physical and chemical properties of peat, the hydrological functioning of different bog types, and the release of nutrients and carbon into porewater and surface waters during the restoration process. This thesis compared forest-to-bog restoration sites to nearby afforested and intact peat at locations in Scotland, examining peat properties, hydrology, and hydrochemistry. In doing so, it attempted to address the main question of how the physical and chemical properties of peat, hydrology and hydrochemistry of porewater and streamwater differ between intact, afforested and forest-to-bog restoration sites on both blanket and raised bogs.

This chapter presents a synthesis of the findings from Chapters 2 – 5. Each chapter's findings are briefly summarised, followed by a more detailed section that discusses potential interactions between findings across different components of the thesis. The discussion will then outline the wider implications of the research, the limitations of the study, and future research priorities. Finally, the chapter ends with an outline of the main implications for management and policy development.

6.2 Summary of key findings

Four main research questions drove the observational and monitoring studies in this thesis. A further question addressed the implications of the research findings for site managers and policy development to restore pre-afforestation ecosystem function whilst minimising environmental impacts from the different restoration processes. This section reports the main findings from previous chapters that examined physical and chemical peat properties, porewater chemistry, hydrological functioning, and streamwater chemistry and chemical fluxes.

6.2.1 Peat properties

Chapter 2 addressed the question, "How do peat physical and chemical properties differ between intact, afforested, and restored raised bogs and blanket bogs?" Overall, bulk density and moisture content were found to differ significantly between intact, afforested, and forest-to-bog restoration sites, but specific yield and hydraulic conductivity did not. I observed that peat at the oldest restoration sites had significantly lower bulk densities and higher moisture content than at the afforested sites. My results suggest that once the partially degraded peat at afforested sites is rewetted, a certain degree of swelling may occur as pores open up, and the peat at restored sites exhibits some of the same hydraulic properties as intact peat. These findings are in line with the peat swelling observed by Anderson and Peace (2017) following re-wetting at afforested blanket bog sites in Halsary and Braehour Forests in Caithness, northern Scotland. The specific yield of peat under mature forest plantations, which would have been above the water table, indicated the peat could still retain significant amounts of water (after being resaturated and allowed to drain) and was not significantly different to the peat sampled from the other treatments. Therefore, this suggests that the peat specific yield was not sensitive to land-use change, and afforested peat may exhibit similar properties to intact peat even after 50 years of forest growth.

Including all sites, the peat carbon content was very slightly but significantly lower in the afforested bogs than the intact bogs, and the restoration sites had higher carbon content than the afforested bogs but lower carbon content than the intact bogs (Table

6-1). Bulk density, moisture content, and humification were significantly correlated with pH, electrical conductivity, and peat depth. Drier surface peat with higher bulk densities generally had lower pH and higher electrical conductivity. Deeper, more highly decomposed peat with higher water content had higher pH and lower electrical conductivity. Carbon content was highest in deeper, more decomposed peat with higher water content. The very slightly lower carbon content of the afforested than intact and restored peat indicates some oxidative carbon losses from the aerated surface peat where the water table was drawn down.

Table 6-1 – A summary of the key variables, including mean water-table depth (cm), the annual water balance totals (mm) and runoff/rainfall coefficient (%), overland flow contribution to total stream discharge (%), medians for the peat properties (0 – 100 cm depths), porewater water chemistry (20 – 80 cm depths), streamwater chemistry and annual fluxes in intact, afforested, and restored bogs. WTD = water-table depth; P = precipitation; Q = discharge; BD = bulk density; Sᵧ = specific yield; K = saturated hydraulic conductivity; von Post = degree of humification on the von Post 1- 10 scale; C = carbon content; EC = electrical conductivity; DOC = dissolved organic carbon; TN = total nitrogen; NH₄-N = dissolved inorganic ammonium as nitrogen; TP = total phosphorus; PO₄-P = dissolved phosphate as phosphorus; Al = dissolved Al; Fe = dissolved Fe; Mn = dissolved Mn; RB = raised bog; BB = blanket bog; R1 = old restored site; R2 = young restored site. The standard error of the mean is given in parentheses. Letters a – d correspond to compact letter displays for significant differences between the sites within the RB and BB locations. Letters the same are not significantly different at the 95% confidence interval.

		RBIB	RBAB	RBR1	RBR2	BBIB	BBAB	BBR1	BBR2
Water table	WTD (cm)	9.8[a] (1.0)	30.6[b] (1.9)	16.0[c] (2.0)	20.7[d] (1.1)	9.6[a] (1.4)	25.6[b] (2.8)	8.4[a] (1.6)	11.9[a] (1.7)
Water balance	P (mm)	1022	1267	1267	1267	1093	1093	1093	1093
	Q (mm)	610	524	673	751	881	688	782	710
	Mean Q (mm d^{-1})	1.7	1.4	1.8	2.1	2.4	1.9	2.1	1.9
	Runoff/rainfall (%)	59.7	41.4	53.1	59.3	80.6	63	71.6	64.9
Overland flow	OLF (%)	19.2	2.9	8.7	34.8	54.6	11.9	32.2	15.4
Peat properties*	BD (g cm^{-3})	0.084[a] (0.002)	0.095[b] (0.003)	0.090[ab] (0.002)		0.093[a] (0.002)	0.098[b] (0.004)	0.094[ab] (0.002)	
	Moisture (%)	90.9[a] (0.2)	89.6[b] (0.4)	90.1[ab] (0.3)		90.3[a] (0.2)	88.1[b] (0.7)	90.0[c] (0.2)	
	Sᵧ	0.076[a] (0.003)	0.078[a] (0.004)	0.089[b] (0.005)		0.071[a] (0.003)	0.071[a] (0.004)	0.063[a] (0.003)	
	K (cm s^{-1})	0.00011[a] (0.0004)	0.00042[b] (0.0003)	0.00004[a] (0.00002)		0.00021[a] (0.0004)	0.00142[a] (0.0003)	0.00039[a] (0.0003)	
	von Post	5.4[a] (0.1)	5.4[a] (0.1)	5.3[b] (0.1)		6.4[a] (0.1)	5.4[b] (0.2)	7.2[a] (0.1)	
	C (%)	51.6[a] (0.1)	51.2[b] (0.1)	51.3[b] (0.1)		51.6[a] (0.1)	51.2[b] (0.1)	51.5[b] (0.1)	
	pH	4.17[a] (0.02)	4.09[a] (0.02)	4.15[a] (0.02)		4.62[a] (0.02)	4.33[b] (0.04)	4.41[b] (0.01)	
	EC ($\mu S\ cm^{-1}$)	24[a] (2.4)	25[a] (0.9)	37[b] (3.3)		19[a] (1.7)	37[b] (2.5)	27[c] (0.8)	
Piezometer	pH	4.00[a] (0.05)	4.01[a] (0.05)	4.12[a] (0.06)	3.99[a] (0.05)	4.58[a] (0.05)	4.41[a] (0.06)	4.43[a] (0.06)	4.06[b] (0.03)
	EC ($\mu S\ cm^{-1}$)	66[a] (1.7)	86[b] (2.4)	64[a] (8.0)	76[c] (3.9)	83[a] (0.9)	182[b] (9.9)	91[c] (3.5)	112[d] (4.4)
	DOC (mg L^{-1})	55.7[a] (1.7)	63.1[b] (2.8)	50.1[a] (2.0)	76.8[c] (3.5)	36.4[a] (1.6)	34.7[a] (2.2)	43.1[b] (1.3)	68.8[c] (2.8)
	NH₄-N (mg L^{-1})	0.56[a] (0.05)	1.29[b] (0.09)	0.25[c] (0.06)	0.67[d] (0.13)	1.13[a] (0.05)	1.96[b] (0.07)	0.14[c] (0.03)	0.36[d] (0.07)
	PO₄-P (mg L^{-1})	0.013[a] (0.016)	0.184[b] (0.028)	0.027[c] (0.024)	0.181[b] (0.075)	0.021[a] (0.004)	0.111[b] (0.016)	0.018[a] (0.003)	0.114[b] (0.061)
Streamwater	pH	4.04[a] (0.17)	3.71[b] (0.02)	5.43[c] (0.04)	4.12[a] (0.05)	4.35[a] (0.05)	4.23[ab] (0.10)	4.31[a] (0.05)	4.09[b] (0.03)
	EC ($\mu S\ cm^{-1}$)	56[a] (4.4)	125[b] (2.6)	45[c] (1.2)	53[a] (4.0)	70[a] (6.0)	155[b] (5.7)	75[a] (10.2)	107[c] (4.6)
	DOC (mg L^{-1})	33.0[a] (3.7)	82.4[b] (1.7)	53.0[c] (1.2)	54.4[c] (6.0)	18.6[a] (2.4)	67.0[b] (6.3)	21.5[a] (2.2)	78.7[b] (5.6)
	TN (mg L^{-1})	0.83[a] (0.14)	2.26[b] (0.16)	0.83[a] (0.60)	1.23[a] (0.18)	0.36[a] (0.06)	1.20[b] (0.14)	0.59[a] (0.12)	1.63[b] (0.20)
	NH₄-N (mg L^{-1})	0.027[a] (0.011)	0.703[b] (0.056)	0.131[c] (0.015)	0.038[a] (0.016)	0.012[a] (0.010)	0.038[a] (0.042)	0.012[a] (0.011)	0.031[a] (0.010)
	PO₄-P (mg L^{-1})	0.004[a] (0.005)	0.154[b] (0.043)	0.022[c] (0.015)	0.051[d] (0.013)	0.004[a] (0.005)	0.282[b] (0.042)	0.005[a] (0.001)	0.238[b] (0.040)
	Al ($\mu g\ L^{-1}$)	40.75[a] (3.8)	178.00[bc] (8.6)	156.00[b] (16.1)	258.00[c] (32.9)	13.90[a] (2.3)	139.50[b] (17.4)	21.50[a] (3.3)	50.95[c] (5.8)
	Fe (mg L^{-1})	0.247[a] (0.04)	2.770[b] (0.16)	1.760[bc] (0.75)	1.780[c] (0.25)	0.074[a] (0.01)	1.030[b] (0.12)	0.124[a] (0.02)	0.416[c] (0.05)
	Mn (mg L^{-1})	0.007[a] (0.002)	0.010[a] (0.002)	0.118[b] (0.397)	0.043[c] (0.005)	0.004[a] (0.001)	0.040[b] (0.013)	0.010[c] (0.002)	0.010[c] (0.001)
Fluxes	DOC flux (kg $ha^{-1}\ yr^{-1}$)	149.8 (14.9)	276.5 (20.8)	220.8 (29.9)	376.5 (36.5)	152.3 (12.0)	308.0 (158.6)	111.7 (16.4)	278.0 (164.9)
	TN flux (kg $ha^{-1}\ yr^{-1}$)	3.36 (0.01)	5.86 (0.01)	3.75 (0.01)	7.23 (0.01)	3.15 (0.01)	5.48 (0.08)	2.44 (0.01)	4.16 (0.07)
	NH₄-N flux (kg $ha^{-1}\ yr^{-1}$)	135.6 (0.04)	637.7 (0.74)	93.1 (0.03)	203.1 (0.01)	93.7 (0.0002)	86.0 (0.01)	118.1 (0.02)	78.5 (0.01)
	TP flux (g $ha^{-1}\ yr^{-1}$)	467.7 (2.02)	574.4 (1.54)	201.8 (0.07)	535.1 (0.11)	91.8 (0.03)	3051.0 (4.14)	213.7 (0.22)	1364.3 (2.38)
	PO₄-P flux (g $ha^{-1}\ yr^{-1}$)	29.0 (0.01)	291.5 (0.34)	55.0 (0.01)	275.7 (0.03)	33.2 (0.00002)	2763.9 (2.79)	46.6 (0.01)	1171.5 (1.26)
	Al flux (g $ha^{-1}\ yr^{-1}$)	192.7 (0.03)	457.5 (0.03)	659.7 (0.36)	1652.8 (1.28)	89.4 (0.004)	685.4 (0.79)	92.0 (0.02)	185.5 (0.07)
	Fe flux (kg $ha^{-1}\ yr^{-1}$)	1.14 (0.002)	6.90 (0.010)	6.93 (0.120)	8.79 (0.060)	0.54 (0.0003)	2.58 (0.030)	0.67 (0.0003)	1.17 (0.003)
	Mn flux (g $ha^{-1}\ yr^{-1}$)	57.4 (0.010)	31.4 (0.001)	815.6 (12.0)	210.1 (0.020)	35.0 (0.001)	123.4 (0.080)	70.8 (0.001)	50.0 (0.0003)

* - Note that the median was taken for the peat properties metrics for each bog type (RB; BB), and the restoration sites are combined into one column.

6.2.2 Peat porewater chemistry

Chapter 3 addressed the question, "How does porewater chemistry differ between intact, afforested, and restored raised bogs and blanket bogs?" Higher electrical conductivity and NH_4-N concentrations, and deeper water tables were associated with the afforested sites. Shallower water tables and greater DOC and PO_4-P concentrations were associated with the restoration sites, especially those most recently restored, as a result of leaching from the brash material left on site, in line with other studies (Asam *et al.*, 2014a; Gaffney *et al.*, 2018; Muller *et al.*, 2015; Rodgers *et al.*, 2010). The highest concentrations of PO_4-P and DOC occurred in the porewater of a restoration site where the felled trees had been mulched, suggesting that the leftover masticated tree debris is a source of PO_4-P and DOC to porewater and ultimately surface waters. However, more research is needed to assess the impacts of mulching on porewater chemistry. At restoration sites where drain and furrow blocking occurred, the mean and seasonal variations in water-table depth were similar to that of the intact bog. Seasonal fluctuations in the water table affected porewater chemistry with greater variability in DOC and nutrient concentrations at shallow depths in the raised bog, where no drain or furrow blocking had occurred. DOC was influenced by peat depth at the raised bog restoration sites with higher concentrations at shallow depths, which I suspect resulted from greater production in the aerobic peat. Previous studies have found that net DOC production increases with temperature and water-table draw-down (Clark *et al.*, 2009). The pH was also lower at shallow depths in the afforested sites at both locations, similar to the depth profiles for pH in the peat cores presented in Chapter 2 (Table 6-1). The drier, more compact surface peat appeared to be a greater DOC source, particularly at the raised bog location. Seasonal trends in DOC are similar to those observed in other porewater studies (Clark *et al.*, 2005; Clark *et al.*, 2008), where it is flushed out in wet conditions following warm periods where DOC production increases. However, the porewater chemistry at both the raised bog and blanket bog locations was similar to the intact bogs at the oldest restoration sites despite the shallower water tables at the blanket bog location.

6.2.3 Hydrological functioning

Chapter 4 addressed the question, "How does hydrological functioning differ between intact, afforested, and restored raised bogs and blanket bogs?" The lower water yield and more subdued streamflow response to rainfall in the afforested bogs than the other treatments suggested the tree stands strongly influence hydrological functioning. The annual runoff-rainfall coefficients at the raised bog location were 59.7% for the intact site, 41.0% for the afforested site (planted year ~1965), and 53.1% for the oldest restoration site (9 years post-felling). The coefficients at the blanket bog location were 80.6% for the intact site, 63.0% for the afforested site (planted year ~1980), and 71.6% for the oldest restoration site (17 years post-felling). Therefore, the oldest restoration sites were most similar to the intact sites at both locations, indicating a potential recovery of hydrological function. Peak storm discharge was significantly greater than in the intact site in the raised bog restoration sites but not for the blanket bog restoration sites. Flow duration curves in the afforested bogs indicate attenuated runoff for all but the top 20% of flows. Water-table peak lag times were greatest, and water-table depths were deepest in the afforested sites and the youngest raised bog restoration site and least in the oldest blanket bog restoration site indicating a recovery trajectory. However, drain and furrow blocking had only taken place at the blanket bog location.

Given that the water table in the restored sites where drains and furrows were blocked was similar to the intact site, we may expect the streamflow dynamics of these sites to be similar, which was confirmed by the greater similarity in the flow duration curves (Figure 4-3) and stormflow metrics (Figure 4-4) between those sites and the intact bog. Overland flow occurred most frequently in the intact sites where the water tables were shallower, while overland flow occurred least frequently in the afforested sites where water tables were drawn down. However, a more frequent occurrence of overland flow in the restoration sites than the afforested sites suggests a potential recovery trajectory towards intact systems. The estimated contribution of overland flow to streamflow in the afforested sites was 2.9% for the raised bog and 11.9% for the blanket bog, increasing to 8.7% and 32.2% at the oldest restoration sites for the raised bog and blanket bog, respectively. Overall, the hydrological functioning at raised bog and blanket bog restoration sites differed from that at the intact sites. However, there was

less difference between the hydrological functioning of intact sites and that at the oldest restoration sites, especially at the blanket bog location where drain and furrow blocking had taken place. Therefore, given that there is likely greater water movement in blanket bogs where slopes can be steeper, this may provide evidence that drain and furrow blocking not only accelerates water-table recovery but may attenuate runoff.

6.2.4 Streamwater quality and fluxes

Chapter 5 addressed the question, "How do streamwater chemistry and chemical fluxes differ between intact, afforested, and restored raised bogs and blanket bogs?" DOC, nutrient and PTE concentrations and fluxes were lowest in the intact sites and highest in the afforested and the recently restored sites. Both DOC and PO_4-P concentrations were highest in the stream draining the afforested bog at the raised bog location. In contrast, at the blanket bog location, streamwater DOC concentrations were highest in the youngest restoration site that had been mulched, while PO_4-P concentrations were highest in the afforested site. However, PO_4-P concentrations at the mulched site were significantly higher than the intact bog and the other restoration sites. Elevated DOC concentrations in the afforested sites could have been due to greater decomposition through deeper water tables. However, the elevated PO_4-P concentrations could result from forest fertilisers leached from phosphorus enriched litter layers in the afforested blanket bog site. Other studies have suggested inputs from fertilisers (Cummins & Farrell, 2003; Drinan et al., 2013b), but elevated concentrations in streamwater following fertilization have only been thought to persist for up to 10 years (Kenttämies, 1981). Low and intermittent flows at the afforested raised bog site likely influenced PO_4-P concentrations, but concentrations were also high at the afforested blanket bog site, where the catchment was larger and continuously flowed throughout the study period.

Al, Fe, and Mn concentrations and fluxes were highest in the streamwater draining the afforested and the most recently restored sites, except at the oldest raised bog restoration site where Mn was highest, possibly from the influence of rock mineral dust from a nearby forest track, which Shah and Nisbet (2019) suggested could have

influenced the streamwater chemistry or disturbances in mineral horizons. Strong positive correlations between DOC and PTE concentrations suggested that DOC was important in their mobilisation because of complexes formed with humic substances (Boggs *et al.*, 1985; Muller *et al.*, 2015; Muller & Tankéré-Muller, 2012) or the reduction of metal-oxyhydroxides through raised water-table levels (Grybos *et al.*, 2009; Nieminen *et al.*, 2015; Nieminen *et al.*, 2017). Annual DOC fluxes at the intact sites were 149.8 ± 14.9 kg ha^{-1} yr^{-1} at the raised bog location, and 152.3 ± 12.0 kg ha^{-1} yr^{-1} at the blanket bog location, which is similar to those from an intact blanket bog site in the Flow Country studied by Gaffney *et al.* (2020). Five to six years post-restoration, annual DOC fluxes were twofold higher than the intact bogs at both locations. However, I observed much lower DOC fluxes of 220.8 ± 29.9 kg ha^{-1} yr^{-1} 9 - 10 years post-restoration at the raised bog location and 111.7 ± 16.4 kg ha^{-1} yr^{-1} 17 - 18 years post-restoration at the blanket bog location. Overall, instantaneous fluxes of DOC and TN did not differ significantly between the different treatments. However, at the raised bog location, instantaneous fluxes of other nutrients and PTEs were significantly higher in the afforested and restored bogs. Fewer significant differences in instantaneous fluxes between treatments were detected at the blanket bog location with only TP, PO$_4$-P, and total and dissolved Fe significantly higher in the afforested and restored sites than the intact sites.

6.3 Integration of findings

The flow of water and solutes in peatlands are closely linked with the peat's physical structure through networks of connected and disconnected pores (Rezanezhad *et al.*, 2016; Zak *et al.*, 2010). Therefore, structural changes in the peat resulting from drainage and afforestation may significantly alter pore connectivity, affecting hydrologic flow pathways and solute transport. Also, a large percentage of flow in intact peatlands has been shown to occur across the surface (Grayson *et al.*, 2010; Holden & Burt, 2003a; Holden *et al.*, 2008), where factors such as surface roughness and the vegetation are important for attenuating runoff. This section aims to assimilate the findings from Chapters 2 - 5 and highlight the important interactions between peat properties, porewater chemistry, hydrology, and DOC, nutrient and PTE fluxes from catchments of the three main treatments: intact bog, afforested bog, and restored bog.

6.3.1 Impact of hydrology on peat properties

The effects of drainage, used to lower the water table (see conceptual diagram, Figure 6-1) and promote tree growth (Chapters 3 and 4), on peat properties have previously been covered in the literature (Holden *et al.*, 2004; Holden *et al.*, 2006; Minkkinen & Laine, 1998; Mustamo *et al.*, 2016) but only one study has looked at changes after forest-to-bog restoration (Anderson & Peace, 2017). Once drains are established, the peat surface is ploughed and planted with trees, further lowering the water table through increased evapotranspiration losses as the trees mature (Anderson *et al.*, 2000; Robinson, 1998). The deepest water tables were observed in the afforested bogs, where evapotranspiration (P – Q) was highest, resulting in lower moisture content and higher overall bulk density (Table 6-1). In this study, the bulk density was significantly higher and moisture content significantly lower (Table 6-1) in the afforested than in the other treatments. Increased pressure from the growing tree stands (Figure 6-1) and the weight of the consolidated surface peat on the buoyant saturated layers below can lead to further shrinkage and consolidation as pores collapse, reducing its permeability and causing the surface to subside (Anderson & Peace, 2017; Price & Schlotzhauer, 1999; Silins & Rothwell, 1998; Sloan *et al.*, 2019). The water table in the restoration sites was closer to that in the intact sites, and as such, moisture and carbon content was higher than the afforested bogs and bulk density lower (Table 6-1) even though the effect was small. The higher carbon content than the afforested bogs in the restoration sites may be evidence of renewed organic carbon accumulation or a loss in inorganic carbon.
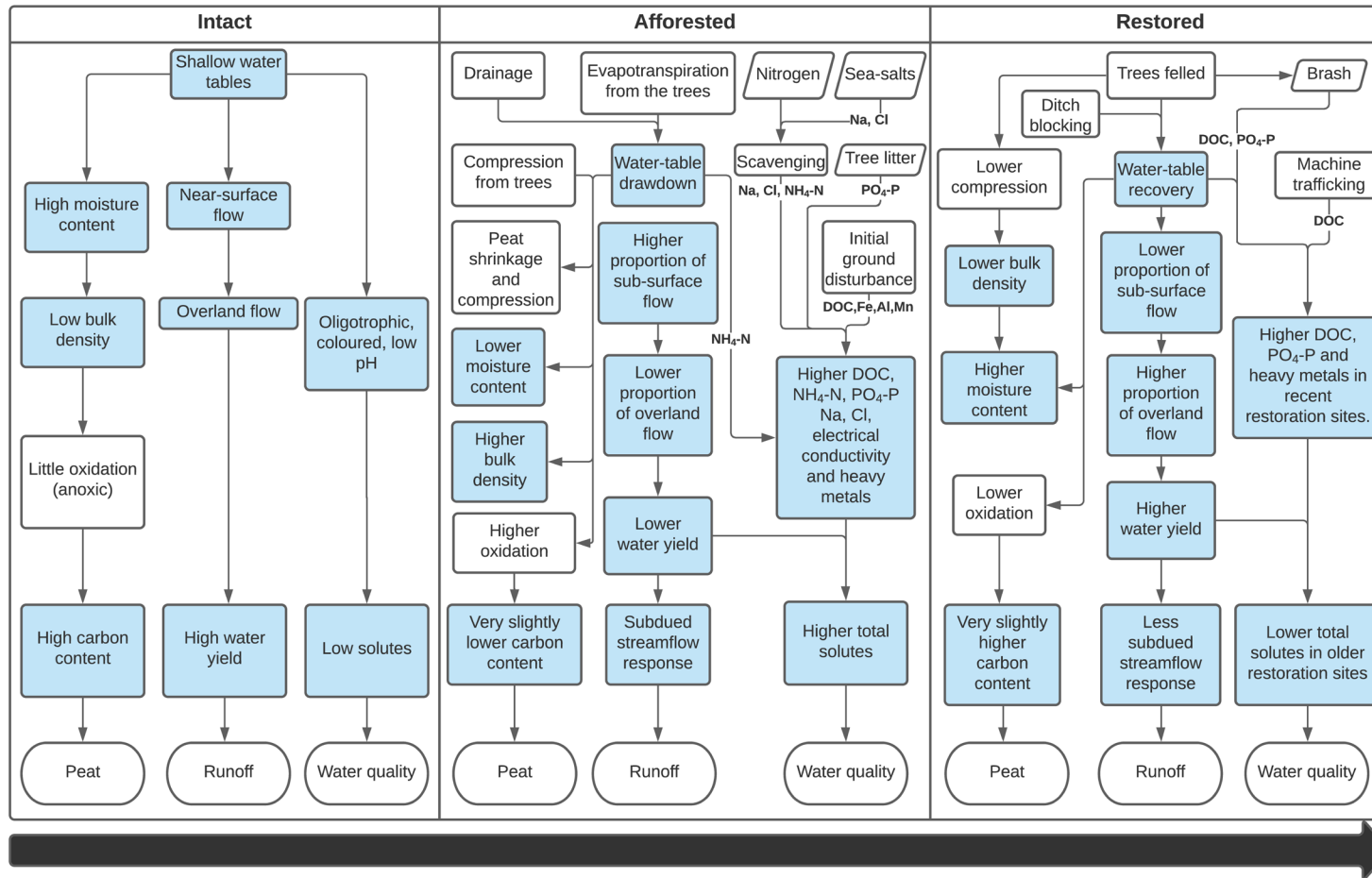
Figure 6-1 – Conceptual diagram of the main processes affecting the peat properties, runoff, and water quality in intact, afforested, and restored bogs, following the research gaps identified in Figure 1-5. The processes highlighted in blue are findings from this study.

The water-table depth varied between intact bog microforms and those associated with forest ploughing in the afforested and restoration sites. Forest ploughing removes 30 - 50 cm of peat below the original surface to form the furrows. Therefore, the top layers in plough furrows would be equivalent to 30 - 50 cm depths from the original surface. Ridges would be a mixture of the peat removed from the furrows. Water tables were deepest in hummocks, followed by lawns and hollows in intact bogs and deepest in ridges and the original surface, followed by furrows in the afforested and restored bogs. There was a greater difference in the humification profiles between afforested microforms than between microforms for the other treatments. The peat in forest furrows was significantly more humified than that in plough ridges and the original surface at greater than 20 cm depths. With time, the furrows can infill with mosses and tree litter, and after restoration, *Sphagnum* recolonisation may be promoted by a rise in the water table, which may explain a convergence in humification profiles in the restored bogs.

In contrast, no significant differences were found between intact bog microforms in this study. In the intact bogs, overland flow was more frequently detected in lawns than in hollows and hummocks, whereas it was mostly detected in furrows in the afforested and restored bogs. Other studies may suggest that peat in hummocks and plough ridges (Baird *et al.*, 2016) would have lower moisture content, higher bulk density, and experience more oxidation than other microforms. Therefore, the resulting peat may be more prone to cracking in plough ridges (Pyatt & John, 1989; Sloan *et al.*, 2018). However, my results did not always follow this pattern when analysing the medians from 122 peat cores. At the raised bog locations, bulk density was highest, and moisture content was lowest in hollows in the intact bog and ridges in the afforested and restored bogs. At the blanket bog locations, bulk density was highest, and moisture content was lowest in hummocks in the intact bogs, which is in line with what might be expected (Baird *et al.*, 2016). However, while moisture content was lowest in the ridges in the afforested and restored bogs, the bulk density was highest in the furrows. The degree of humification was highest in the hummocks in the raised bogs, highest in hollows in the blanket bogs, and greater in the furrows in the afforested and restored bogs. Therefore, there was significant variability between the different surface features

in the intact, afforested and restored bogs in this study and stronger patterns were not observed with a larger number of peat samples, contrary to what Baird *et al.* (2016) suggested.

6.3.2 Impact of peat properties on hydrology

The physical properties of the peat will also affect hydrology. The porosity and hydraulic conductivity may affect the subsurface flow and water-table response to rainfall. In this study, saturated hydraulic conductivity ranged from 2.67×10^{-3} cm s^{-1} to 5.53×10^{-7} cm s^{-1}, similar to values reported in other studies (Baird *et al.*, 2016; Lewis *et al.*, 2012; Päivänen, 1973), but there was no significant difference between treatments, contrary to other studies where lower values have been associated with afforested peatlands (Päivänen, 1973; Silins & Rothwell, 1998). Silins and Rothwell (1998) ascribed changes to peat hydraulic properties after drainage and afforestation to the collapse of macropores. The 32 mm diameter peat sub-samples taken for laboratory analysis may have contained smaller macropores, but larger tree roots were not present. However, it is possible tree roots would have been included in the field measurements of hydraulic conductivity, which, along with surface cracking, may explain the higher permeability of the afforested peat. The degree of humification has also been found to influence water flow in the peat matrix (Päivänen, 1973), with the porosity decreasing as larger fragments of plants are broken down into amorphous peat (Rezanezhad *et al.*, 2016). Despite no significant difference in hydraulic conductivity and specific yield between treatments (Table 6.1), both displayed significant negative correlations with von Post humification, indicating control of humification on matrix flow. The peat may be expected to be more humified in afforested bogs after the disruption caused by ploughing and drainage and deeper water tables leading to more aeration. Surprisingly, this was only observed in the top 10 cm when comparing treatments (Figure 2-2). Therefore, except in the top 10 cm, subsurface flow through the upper layers of peat may not differ significantly between treatments. This finding may explain why the flow duration curves were comparable between intact, afforested, and restored treatments at the blanket bog location (Figure 4-3). It may be that the presence of flow along pore spaces created by larger tree roots and surface desiccation cracks compensated for any macropore closure through afforestation.

Surface infiltration rates for the raised bog and blanket bog afforested sites were not significantly different (Table 6.1), suggesting that other factors such as tree age influenced the water-table dynamics presented in Section 4.3.3. The trees were older at the afforested raised bog site, and it was slower to reach a water-table peak in response to rainfall events than the afforested blanket bog. Furthermore, the magnitude of the rise in the afforested bogs was typically greater at the raised bog location, probably due to deeper initial water tables resulting from higher evapotranspiration rates. Reduced moisture content and lower water tables at the afforested sites led to more subdued streamflow dynamics than the intact bogs and less overland flow (Figure 6-1). The differences in peat properties observed between the raised bog and blanket bog sites outlined in Chapter 4 may also have influenced the water-table recovery at both locations. The lower bulk density, specific yield, very slightly higher moisture, and organic matter content at the blanket bog location could suggest that the peat was more porous and retained moisture for longer than at the raised bog location. However, the differences were small, and on average, the peat was more humified at the blanket bog location.

The degree of humification may also influence the water-table response to rainfall. Results presented in Chapter 4 suggested that peat in the afforested sites experienced a greater rise in the water table during storms, possibly because the peat was denser and more humified in the upper layers, and there were fewer voids for the water to fill. However, other studies have found the water table in more humified peat to rise quicker with rainfall and fall faster after it ceases (Taufik *et al.*, 2019), which was not observed in this study. Specific yield and the time taken for the water table to rise by 1 mm were also not significantly different between sites. Therefore, the greater water-table rise in the forestry likely resulted from the fact that the water table was more drawn down, and therefore, there was more water storage capacity available.

Given the small magnitude of differences in peat properties, overland flow may be more important than subsurface flow in restoration catchments after re-wetting.

Although I found the streamflow to be largely dominated by sub-surface flow (following hydrograph separation), the proportion of overland flow was greater in the older restoration sites (Figure 6-1) than the afforested bogs at both raised and blanket bog locations. Overland flow occurred more frequently at the blanket bog location, but the percentage change in the overland flow contribution to total discharge between the afforested and the older restoration sites was greater at the raised bog location. In contrast, there was no big difference in hydrological function between the intact and restored sites at the blanket bog location. The greatest differences were observed between the afforested and intact sites at both locations, most likely a consequence of the water-table position and the effects of drainage and evapotranspiration than differences in the peat properties.

6.3.3 Impact of peat properties and hydrology on pore and streamwater chemistry

Solutes may be transported by advection through networks of connected pores within the peat or attenuated by molecular diffusion into unconnected, dead-end pores and by sorption and degradation reactions for reactive species (Rezanezhad *et al.*, 2016). Water may also flow across the peat surface where there may be other sources of solutes and particulates (e.g., brash/bare peat). Much surface flow in peatlands has been shown to occur as saturation-excess overland flow facilitated by shallow water tables (Evans *et al.*, 1999; Holden & Burt, 2003b). Chapter 4 showed that overland flow was most likely to occur in intact bogs and least likely in afforested bogs. Shallower water tables after forest-to-bog restoration were evident in Chapters 3 and 4 and other studies (Anderson & Peace, 2017; Gaffney *et al.*, 2018; Muller *et al.*, 2015) and coincided with a greater occurrence of overland flow, recorded by crest-stage tubes between site visits (Figure 6-2), in restored compared to afforested sites. There were significant negative correlations between water-table depth and overland flow occurrence for intact ($r_s = -0.270$, $p < 0.001$, $N = 311$), afforested ($r_s = -0.423$, $p < 0.001$, $N = 214$) and restored ($r_s = -0.426$, $p < 0.001$, $N = 530$) treatments.
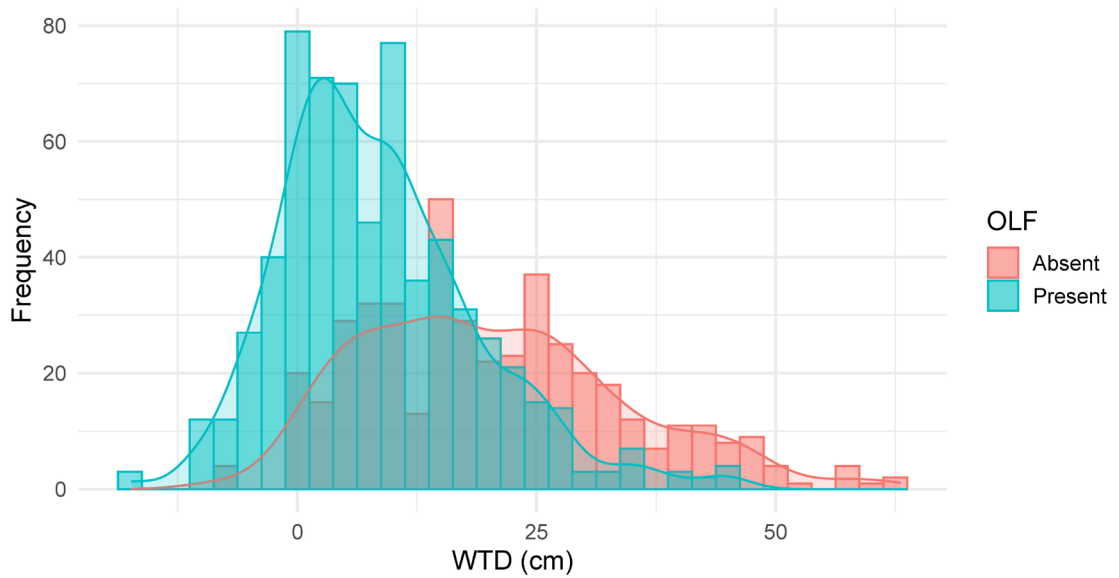
Figure 6-2 – Distribution of overland flow detected between site visits with respect to water-table depth (WTD) at all study sites.

Deeper and more fluctuating water tables associated with the afforested sites were associated with higher NH_4-N concentrations in the porewater (Table 6-1), as Gaffney et al. (2018) reported. However, there was a greater distinction between the shallow and deep porewater sampling depths at the blanket bog location (Figure 6-3). Increased ammonification through deeper water tables in the forestry likely explained the higher NH_4-N concentrations in the porewater. However, the low streamwater NH_4-N concentrations (Table 6-1), and NO_3-N concentrations, mostly below the detection limits, indicate that any excess nitrogen was quickly taken up by the vegetation (Howarth, 2014; Urbanová *et al.*, 2011). DOC and PO_4-P concentrations were sometimes higher in the streamwater than the porewater at the afforested sites, suggesting inputs from surface water flowing through the brash and litter layers (Table 6-1). Seasonal variability in DOC was highest in the streamwater draining afforested and restored bogs at the blanket bog location, likely flushed out during wet periods following warm spells, possibly due to greater water and solute movement from the marginally steeper slopes at the blanket bog location (Figure 6-3).
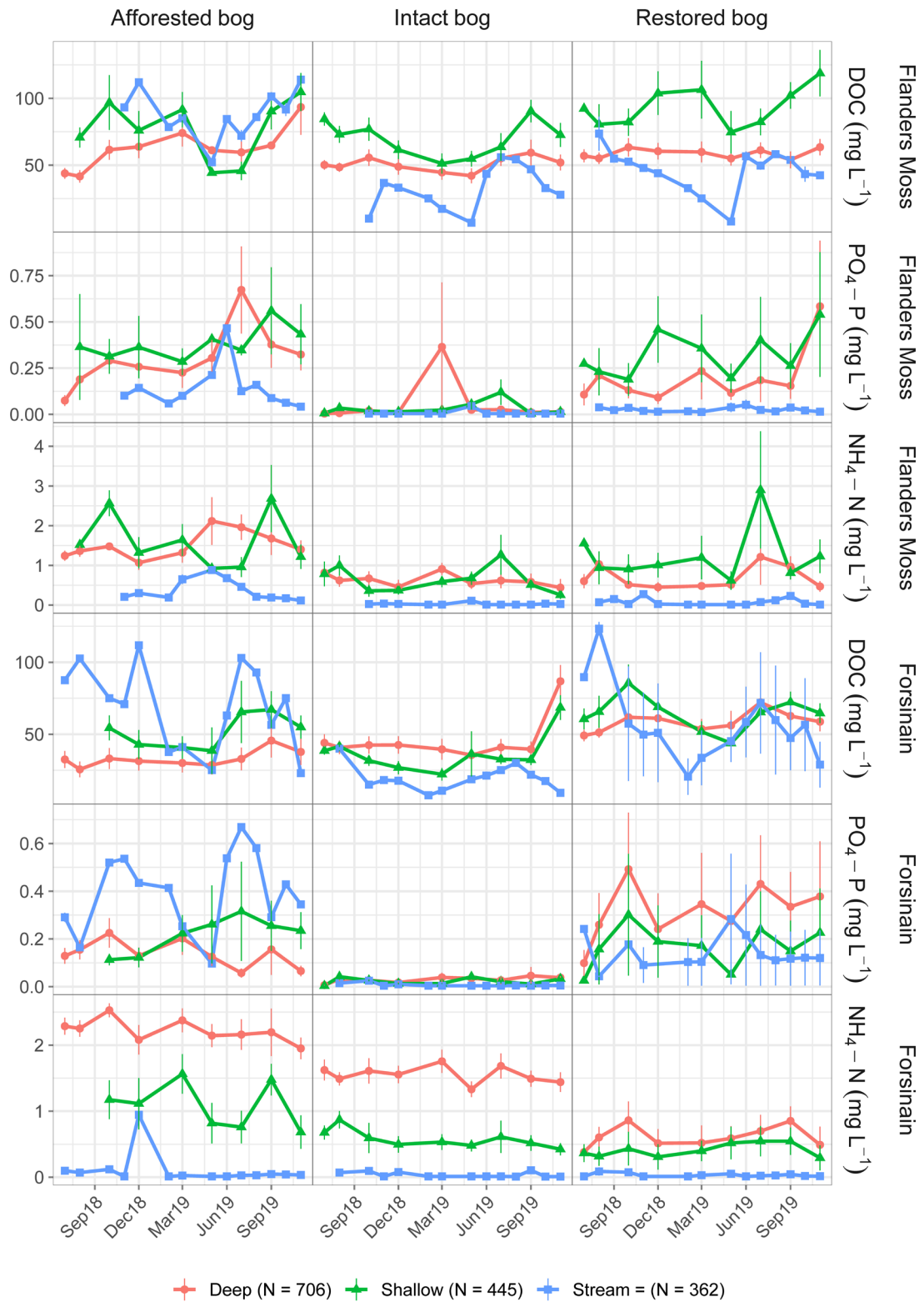
Figure 6-3 – DOC, NH₄-N, and PO₄-P concentrations ± SE for shallow (20-40 cm) and deep (60-80 cm) porewater and streamwater for the three main treatments for Flanders Moss (raised bog) and Forsinain (blanket bog). Concentrations are taken as the mean of the piezometer nests and streamwater samples for the different treatments.

The transport of solutes will be affected by changes in the near-surface peat properties, whereas solutes are more likely to be retained in deeper anoxic layers except where macropores and soil pipes are present. The acidity and electrical conductivity were greater in the shallow porewater depths and controlled by the pH and electrical conductivity of the peat. For example, peat pH and porewater pH were most strongly correlated ($r_s = 0.760$, $p < 0.001$, $N = 31$) in the intact bogs, whereas peat and porewater electrical conductivity were most strongly correlated ($r_s = 0.518$, $p = 0.009$, $N = 24$) in the afforested bogs (Figure 6-4). A positive correlation was observed between peat pH and depth below the surface ($r_s = 0.342$, $p < 0.001$, $N = 966$), and a negative correlation with peat electrical conductivity and depth ($r_s = -0.282$, $p < 0.001$, $N = 966$), which was also reflected in the porewater at the raised bog restoration sites (Chapter 3). The peat pH generally increased at deeper, more humified peat depths, whereas peat electrical conductivity decreased with depth. A reduction in the peat bulk density and an increase in the specific yield could lead to greater transport of solutes shortly after restoration, which could have environmental implications for water quality. However, lower porewater and streamwater DOC and PO_4-P concentrations were observed at the oldest rather than the youngest restoration sites, most likely as solutes derived from the brash were depleted.
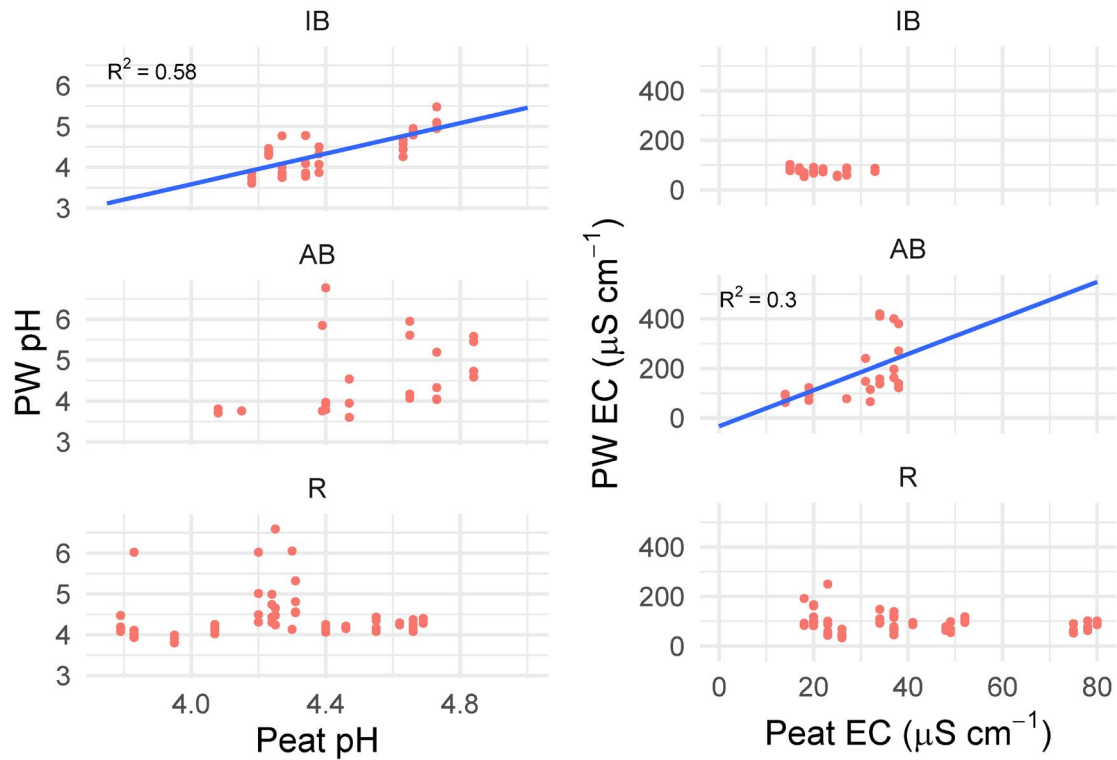
Figure 6-4 – Relationship between porewater (PW) and peat pH and porewater and peat electrical conductivity (EC) at the time of peat core sampling. The mean was taken of the piezometers and peat cores at 20, 40, 60 and 80 cm depths for each treatment where IB = intact bog, AB = afforested bog, and R = restored. The lines represent significant correlations at the 95% confidence interval.

Streamwater pH and electrical conductivity displayed few relationships with porewater pH and electrical conductivity from different peat depths except at the intact sites (Figure 6-5), where the strongest correlations occurred at 20 and 40 cm (shallow depths). Figure 6-5 also illustrates that the range in porewater and streamwater pH was greater for the intact and restored sites than the afforested sites, where the pH range was small. Electrical conductivity was much lower in the porewater in the intact bogs than in the other sites, and there was a greater range in values at the afforested and restored sites. Streamwater draining the afforested bogs had consistently higher electrical conductivity than the intact and restored bogs, and the range of values in the restoration sites varied from high to low in both porewater and streamwater.
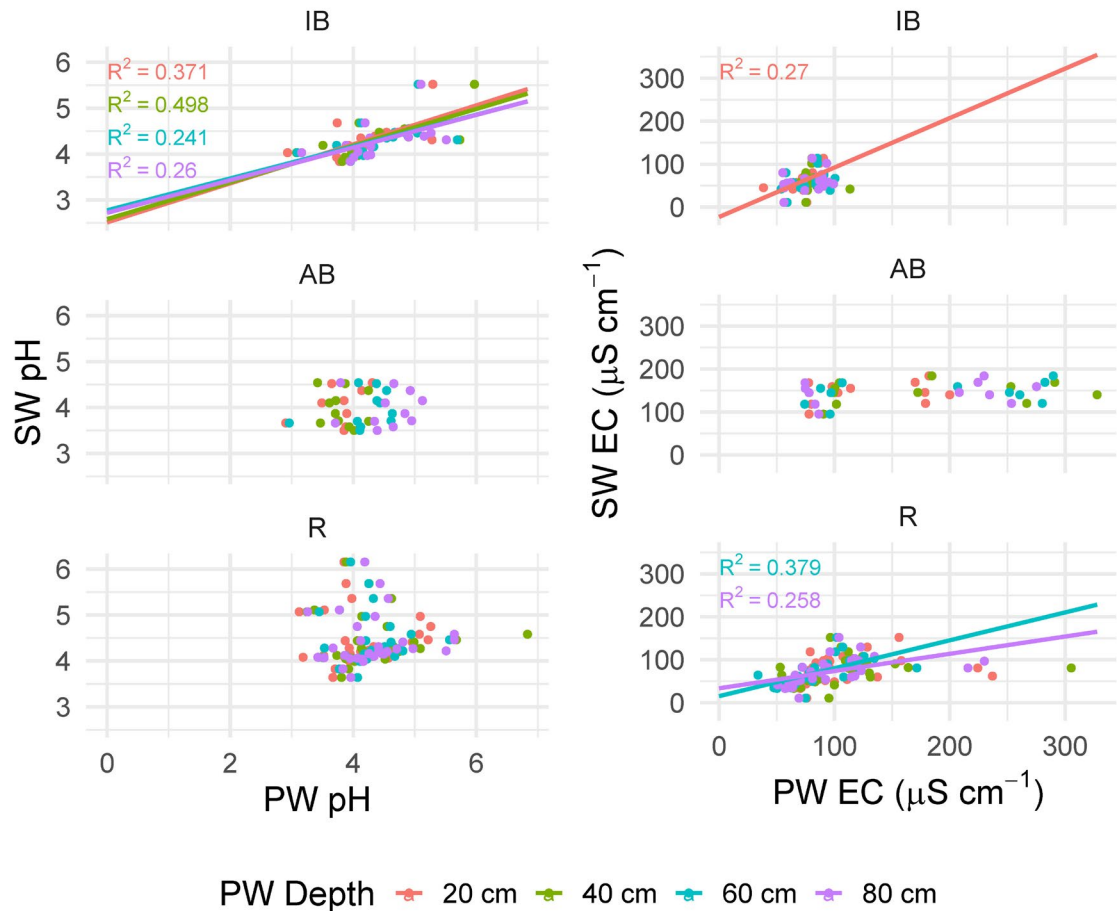
Figure 6-5 – Relationships between mean streamwater (SW) pH and electrical conductivity (EC) for the three treatments, plotted against porewater (PW) pH and EC on the same sampling date. The mean was taken of the piezometers for the three treatments at 20, 40, 60 and 80 cm depths. The separate lines represent significant correlations at the 95% confidence interval for the different porewater sampling depths.

Hydraulic conductivity and specific yield were not significantly different between treatments. Therefore, there was little difference in the water retention capacity and the sub-surface flow velocity that may influence solute transport. Higher water-tables and increased overland flow in the restoration sites may mean more solutes will be picked up from flowing across the surface than through the peat matrix, although water flowing over the surface of other soils have been found to contain inputs from the porewater (Ahuja *et al.*, 1981; Mulqueen *et al.*, 2004). Therefore, it may be assumed that streamwater at the intact sites would reflect the shallow porewater chemistry as the water tables were shallowest at these sites, whereas streamwater draining the afforested catchments may be more similar to the chemistry of the porewater from deeper depths. However, I found this was variable between the different treatments, making it difficult

to establish a link between the porewater and streamwater concentrations (as illustrated for DOC in Figure 6-6), possibly due to less intensive porewater sampling in the riparian zone (Billett *et al.*, 2006; Clark *et al.*, 2008). Figure 6-6 illustrates the wider range of DOC and PO_4-P concentrations in porewater and streamwater at the afforested and restoration sites than intact bogs. The wider range of DOC and PO_4-P concentrations at the restoration sites than the other treatments and few strong correlations may illustrate the influence of overland flow on streamwater DOC and PO_4-P. On average, TOPMODEL analysis showed that the proportion of overland flow to total streamflow was 15.9% greater in the older restoration sites than the afforested bogs, which may collect solutes and particulates from the brash on the surface. There was greater linearity for DOC in the afforested bogs, suggesting where the water table was drawn down, the streamwater chemistry reflected the porewater chemistry more, but where water tables were high, the overland flow was more important. The correlations between streamwater and porewater concentrations at deeper depths in the restoration sites may suggest that the streamwater was influenced by the deeper porewater when water tables were deeper. However, the absence of correlations between streamwater and shallow porewater may suggest that when water tables were shallower, solutes were collected from flow across the surface, mixing with forest residues.
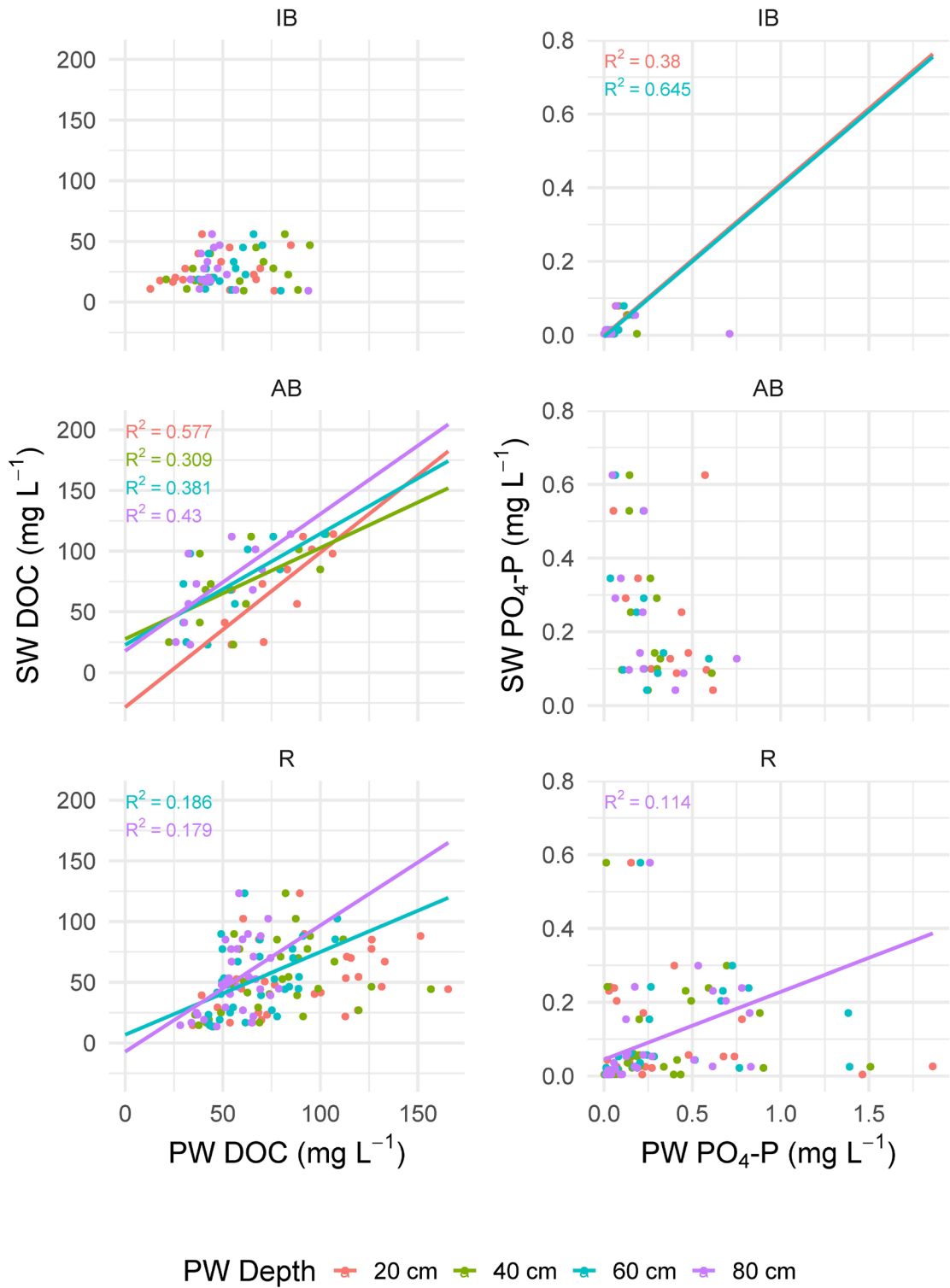
Figure 6-6 – Relationships between mean streamwater (SW) DOC and PO₄-P concentrations for the three treatments, plotted against porewater (PW) DOC and PO₄-P concentrations on the same sampling date. The mean was taken of the piezometers for the three treatments at 20, 40, 60 and 80 cm depths. The separate lines represent significant correlations at the 95% confidence interval for the different porewater sampling depths.

The lower pH of the peat and porewater in the afforested and restoration sites than at the intact sites (Chapters 2 and 3) indicates the legacy of acid interception (Dunford *et al.*, 2012; Neal *et al.*, 1992; Neal *et al.*, 2004; Nisbet *et al.*, 1995) from forest canopies and acidic forest litter inputs (Figure 6-1). However, differences in peat pH between the intact, afforested and restored sites varied between the two locations; differences were insignificant between sites at the raised bog locations and highly significant between sites at the blanket bog locations. Electrical conductivity in the peat, porewater and streamwater was highest in the afforested sites, particularly at the blanket bog location, which was closest to the sea. However, only electrical conductivity in porewater from 60 cm depth was significantly correlated with that in streamwater ($r_s = 0.629$, $p = 0.12$, $N = 15$). Higher electrical conductivities at the afforested and restoration sites (Figure 6-1) could be due to legacy effects of sea-salt scavenging (Dunford *et al.*, 2012; Harriman *et al.*, 2003; Neal *et al.*, 1992; Reynolds *et al.*, 1994) by forest canopies, felled tree debris and litter inputs. Variable differences in peat, porewater and streamwater pH between the different sites suggest that both sea-salt scavenging and forest materials were likely sources, depending on the site. However, higher streamwater Na and Cl concentrations at the afforested bog closest to the sea highlighted the influence of aerosol scavenging.

6.3.4 Impacts of the hydrology on chemical fluxes

The fluxes of soluble carbon, nutrients, and PTEs were generally highest from sites where the streamwater concentrations were highest, and the annual discharge was lowest except in the youngest raised bog restoration site. Thus, annual fluxes from the afforested sites were often higher than those for the other treatments, suggesting that nutrient cycling changes due to afforestation drove the differences in fluxes between sites. However, seasonal patterns of discharge controlled instantaneous flux patterns for much of the year at the blanket bog location. The youngest raised bog restoration site, which was also the largest by area, had the highest annual DOC, TN, Al, and Fe fluxes and more pronounced seasonal patterns of instantaneous fluxes. During storms, the magnitude of increased discharge was often greater than the decline in concentrations in this catchment, as observed by Clark *et al.* (2007). Surface brash may be a source of

PTEs (Asam *et al.*, 2014a; Kaila *et al.*, 2012), but the youngest restoration sites had similar seasonal streamwater concentrations and fluxes for Fe, Al, and Mn as the intact and the older restoration sites, which suggests ground disturbance is a more likely source in the restoration sites in this study. Therefore, fluxes of DOC and PO_4-P may be influenced by flow over the surface and near-surface peat-brash interactions, and the fluxes of PTEs may be influenced by water mixing with the deeper horizons and a consequence of water-table recovery in the restoration sites.

6.4 Implications of findings

6.4.1 Implications of restoration for water supply, riverflow regime, and flood risk

The higher runoff-rainfall ratios in the restoration sites than the afforested bogs suggest an increased likelihood of higher river flow peaks after restoration. However, our results did not provide conclusive evidence forest-to-bog restoration sites would lead to higher river flow peaks than intact bogs, but the restoration methods varied between sites. The vegetation, particularly *Sphagnum* mosses, and natural microforms associated with intact bogs have been shown to attenuate overland velocities (Grayson *et al.*, 2010; Holden *et al.*, 2008). However, the vegetation (Section 4.4.1) and natural microforms differed between the restored and intact sites, which also affected the occurrence of overland flow (Section 4.3.4). In addition, overland flow at the restoration sites is likely to have been channelled down the plough furrows. Therefore, furrow blocking may be an important step in attenuating runoff after forest clearance. The addition of new peat dams in the main drain at the youngest blanket bog restoration site led to lower peak flows than before their installation, and the similarity in flow duration curves between the blanket bog treatments suggest they were an important factor in controlling runoff (Section 4.4.2). So far, no substantial planting and seeding efforts have been used to support the regeneration of peat-forming plant species at any forest-to-bog restoration sites I am aware of; they have been left to recolonise naturally. Therefore, other interventions such as plug planting or spreading of *Sphagnum* mosses (Evans & Shuttleworth, 2019; Lunt *et al.*, 2010; MFTFP, 2020) may be necessary to restore the same mixture of bog species as intact bogs, which would reduce overland flow velocities and river flow peaks (Gao *et al.*, 2016). The water yield associated with forest-to-bog restoration > 17 years after restoration was

similar to intact bogs and greater than afforested bogs at the blanket bog location. Therefore, the results suggest that water yield will be greater after restoration, but the effects on low flows, especially at sites where drain and furrow blocking has occurred, suggest mean water supplies in dry periods will be reduced.

6.4.2 Implications of restoration for downstream water quality

As indicated by the electrical conductivity, total solutes were higher in streamwater draining the afforested sites, likely because of the increased capture of aerosols in the forest canopies. Higher nitrate concentrations have been observed in streamwater shortly after felling (Gaffney *et al.*, 2018; Shah & Nisbet, 2019), but concentrations were below the detection limits for most samples in my study. Results from my study suggest that nitrogen enrichment of streamwater through forest-to-bog restoration is unlikely to be an issue for freshwater ecology and more of an issue for the restoration of minerotrophic fens (Koskinen *et al.*, 2017; Sallantaus & Koskinen, 2012) where the higher pH and nutrient content of the fen peat would lead to greater NH_4-N and NO_3-N production (Koskinen *et al.*, 2017).

DOC and PO_4-P concentrations in the porewater and streamwater were significantly higher in the youngest restoration sites than in the intact bogs. DOC concentrations were twice as high in the porewater and four times higher in the streamwater in the youngest blanket bog restoration site, where trees had been mulched, and PO_4-P was five times higher in the porewater and 60 times higher in the streamwater in the same site (Table 6-1). Porewater concentrations of PO_4-P were significantly higher in drains and furrows where brash had accumulated than porewater from where it had not, which reinforces reports of PO_4-P leaching from brash to surface waters by other studies (Asam, 2012; Asam *et al.*, 2014b; Gaffney *et al.*, 2018; Rodgers *et al.*, 2010). Therefore, results suggest that removing all trees and brash from the restoration sites is likely to have a lower impact on streamwater quality than if left on site (Shah and Nisbet, 2019), used to block furrows and drains or mulched and spread across the peat surface. However, further research is needed to assess the impact of mulching on water

quality fully. Forest-to-bog restoration is likely to have the most impact on freshwater systems that contain species sensitive to changes in nutrient concentrations, such as populations of Atlantic salmon and freshwater pearl mussel, highlighted by Shah and Nisbet (2019) or macroinvertebrate assemblages where outflows are into oligotrophic lakes (Drinan *et al.*, 2013a; Drinan *et al.*, 2013b).

In this study, the peat carbon content was very slightly but significantly higher in the restored than the afforested sites, suggesting less carbon loss through aerobic decomposition or renewed carbon sequestration after clear-felling re-wetting. However, DOC fluxes may be higher than afforested bogs in the early stages of restoration, some of which may be later lost to the atmosphere (Palmer *et al.*, 2015), which must be remembered when considering the climate change mitigation potential of forest-to-bog restoration. Increases in DOC concentrations will also be a concern for water companies who spend a significant amount of money removing it from drinking water (Price *et al.*, 2016), and there have been health risk concerns associated with trihalomethane compounds (THMs) produced in the water treatment process (Singer, 2006). However, > 17 years after restoration, the aquatic DOC flux from the blanket bog was not found to differ significantly from that from the intact bog; therefore, there is a trade-off between higher short-term environmental impacts of restoration and the long-term carbon sequestration benefits. The water-table depth and streamflow dynamics were closer to the intact bog in the same location where a combination of furrow and drain blocking had occurred. Overall, all the signs indicate the hydrology and hydrochemistry of forest-to-bog restoration sites after 10+ years move closer toward intact systems, and any environmental risks are relatively short-term.

6.4.3 Implications of restoration at raised bogs and blanket bogs

Water tables were shallower at the blanket bog than the raised bog sites, and there was less difference in streamflow metrics, and flow duration curves between the different treatments, which I believe is due to the drain and furrow blocking that took place at the blanket bog location. The streamwater and porewater chemistry at the blanket bog location were comparable between the oldest restoration site and the intact site, but the

streamwater draining of the oldest raised bog restoration site had a much higher pH and PTE concentrations than the intact site. Stream and porewater DOC concentrations were significantly higher at the raised bog sites than the blanket bog sites (Table 6-1), suggesting steps to attenuate flow might be necessary to avoid greater aquatic carbon losses, as evident at the youngest raised bog restoration site in this study. Generally, the porewater chemistry seemed similar after restoration at the raised and blanket bog locations. However, streamwater concentrations of Al, Fe and Mn were significantly higher at the raised bog location, which most likely relates to the level of disturbance at this site and not necessarily a reflection of a difference between raised bogs and blanket bogs. Raised bogs typically have much gentler slopes than blanket bogs. At the Flanders Moss National Nature Reserve, the elevation change is often < 6 m over a 1 km distance. Therefore, the hydrology differs between raised and blanket bogs, with higher runoff-rainfall coefficients and overland flow frequency observed at the blanket bog sites. The slopes of the raised bog and blanket bog sites in this study were roughly similar, with marginally steeper slopes at some of the blanket bog sites. However, steeper slopes on either side of a stream at the largest raised bog site may explain the higher contribution of overland flow to total streamflow than the other raised bog sites, which was not detected at the crest-stage tube locations. Therefore, at other sites where steeper slopes are commonly found, drain and furrow blocking may become more important.

Both bog types had significantly higher water tables in the restoration sites than the afforested bogs, and a similar water-table response to restoration should be expected in both bog types. The maritime proximity of the study sites also influenced the porewater and streamwater chemistry by capturing sea salts in the afforested bogs, particularly at the blanket bog location, which was ~14 km from the coast compared to ~60 km at the raised bog location. Elevated electrical conductivity, Na and Cl concentrations were observed at the blanket bog location and to a lesser extent at the raised bog location. However, the wider survey of peat properties from two raised bog and two blanket bog locations also suggests local differences between sites may sometimes be more important than bog type and land-use change.

6.5 Limitations of the study

I believe this study provided a rich dataset over several seasons and sites to analyse many of the key variables affected by afforestation and subsequent forest-to-bog restoration and provided a good overall picture of some of the key issues. However, several inevitable limitations were encountered. First is the lack of true catchment replicates, which is difficult in many field studies due to time constraints and costs but having further replicates would have reduced the level of uncertainty. Also, using a chronosequence approach, the effects in the early stages of restoration could not be measured. For example, the practice of mulching may have implications for nutrient enrichment of soil and streamwater, but at the time of my study, much of the nutrients in the woodchip debris would likely have been depleted, and the study lacked replicates of mulched restoration sites. Given the brash-surface flow interactions, especially in furrows and drains, they may be an important source to receiving streams and were something we did not measure in this study. We found high porewater concentrations in furrows where brash had accumulated, but we did not analyse concentrations from the crest-stage tubes.

I opted to use a space-for-time substitution rather than a before and after study, which comes with limitations, but it would have been impossible to infer longer-term changes associated with the restoration without this design. If there were no time limits, a long term study would be recommended, similar to the afforestation study of the Coalburn catchment in Northumbria (Robinson, 1998). The choice of using small catchments came with limitations since low flows influenced streamwater flows and concentrations, but having the study coincide with one of the driest summers on record was unavoidable and could be viewed as an opportunity to gain insights into how similar catchments might respond to our changing climate. Where low flows are less of an issue in larger catchments, it is more difficult to select a catchment that represents the land use, and soil types and the geology may vary over larger areas. Therefore, selecting catchments representing the same land use, geology, and soil type, with sufficient flow over the year, is important in studies of this nature. Furthermore, the stream outflow at one site was close to the River Forth, which is known to back up during high flows, resulting in higher streamwater levels than usual. Therefore,

streamwater depth readings and solute concentrations may occasionally have been affected.

In this study, problems with inferring any differences between blanket bogs and raised bogs are that drains and furrows were only blocked at some of the blanket bog restoration sites and not at the raised bog restoration sites. The distance between study site locations was sometimes ~250 km, and, therefore, local environmental conditions would have differed. The trees had also been planted earlier at the raised bog location and had grown larger, perhaps partly explaining the difference in solute exports and hydrological function, although it is difficult to determine without a more focused study on these effects. The differences between the peat properties in intact sites also suggested that local differences between sites can also be greater than those of the land-use change. Therefore, these confounding factors need to be considered in similar studies.

6.6 Directions for further study

The following areas of research are recommended in order to further advance the understanding of forest-to-bog restoration on the hydrology, peat properties and hydrochemistry beyond that contributed by this project:

1. Microscopic analysis of peat pore structure from intact, afforested and restored peat would improve the understanding of structural peat changes with the land-use change.

2. A fully replicated study is required to assess the impact of mulching on phosphorus concentrations in porewater and streamwater and whether it poses downstream environmental risks.

3. An assessment of whether fertiliser use in afforested peatlands can still be a phosphorus source greater than 10 years after application would improve the understanding of nutrient enrichment after forest-to-bog restoration.

4. A fully replicated study on drain and furrow blocking with forest-to-bog restoration would determine their efficacy in raising the water-table level, attenuating flow and reducing solute fluxes.

5. A fully replicated study on some of the newer forest-to-bog re-wetting treatments such as 'stump flipping'/ground smoothing and methods to re-wet cracked peat is needed.

6. Currently, I am unaware of any additional planting or reseeding efforts to promote the recolonisation of forest-to-bog systems despite its use in other programmes of peatland restoration. Therefore, a new study to determine if it could improve restoration outcomes would be useful.

7. Given the increase in overland flow due to forest-to-bog restoration, an assessment of the downstream contribution of solutes from overland flow would improve the understanding of solute transport after forest-to-bog restoration.

8. A more detailed study is needed that considers the characteristics of the trees such as species, age, height, and canopy growth on the peat properties, hydrology and water chemistry.

9. A forest-to-bog restoration study of the resulting runoff covering a range of slope conditions typically found in blanket peatlands may be necessary at more undulating sites.

10. A full assessment of soil carbon stocks that considers differences in the degree of oxidative wastage/shrinkage and compression following afforestation is necessary if carbon losses associated with afforestation and potential carbon gains through forest-to-bog restoration are to be understood.

11. More evidence is needed on sites that have been through more than one forest cycle to determine the optimum time to restore afforested peatlands considering the carbon balance between the peat and the above-ground biomass.

6.7 Implications for management

In answer to the research questions, we found significant differences in the peat properties, hydrological function, porewater and streamwater chemistry between intact, afforested and restored bogs. Overall, many differences were not large, except for DOC, PO_4-P and PTE fluxes and runoff-rainfall coefficients between the afforested and

most recent restoration sites and the intact bogs. Our results suggest that elevated DOC and PO_4-P concentrations in porewater and streamwater may persist for longer than those studied by Shah and Nisbet (2019), who found PO_4-P streamwater concentrations may still be elevated 6 – 7 years and DOC 3 – 4 years following forest clearance. However, the latter study did not make comparisons with intact bogs. Potentially, mulching may negatively affect water quality, but downstream water quality concerns will likely be more of an issue shortly after clear-felling (Gaffney *et al.*, 2021). Results indicated that peat in the older restoration sites was similar but not the same as intact peat, and the afforested peat sometimes displayed similar hydraulic properties to intact peat. Hydrological function in the afforested bogs was mostly influenced by drainage and evapotranspiration, which lowered water tables and subdued streamflow response to rainfall. It is clear from this and other studies that restoration achieves the objective of raising water tables through clear-felling, and when used together with drain and furrow blocking, it may result in water-table levels in line with intact systems. Water-table and streamflow changes with rainfall were not the same in restoration sites as intact systems, but there was less difference where drain and furrow blocking had been used in conjunction with clear-felling.

The main differences between treatments for porewater and streamwater solute concentrations were for PO_4-P, DOC, and PTEs after clear-felling, although high streamwater concentrations were also detected in the afforested bogs compared to intact sites. Felled waste appears to be a significant source of PO_4-P and soluble carbon in both the porewater and streamwater even five years after restoration, and mulched debris may be a significant source. Much higher PO_4-P concentrations have been reported shortly after restoration, and DOC is also known to facilitate the transport of PO_4-P, which has implications for the phosphate sensitive freshwater pearl mussel. Also, increases in PTEs have previously been linked to declines in Atlantic salmon. It is also possible that the elevated streamwater PO_4-P concentrations in the forestry may have been a consequence of forest fertilisers, but records of their application were unclear. However, 17+ years following restoration, the differences between a blanket bog restoration site and an intact site, from my study and a study by (Gaffney *et al.*,

2018), were found to converge. Therefore, the key factors in minimising the potential negative impacts of forest-to-bog restoration on water quality are handling felled waste and avoiding additional soil disturbance that may influence streamwater chemistry. Recommendations for management are:

1. Furrow and drain blocking are strongly recommended as part of forest-to-bog restoration to assist in the water-table recovery and runoff attenuation.
2. Low impact harvesting and phased felling should be used to reduce water quality impacts in the early stages (also demonstrated by Shah & Nisbet, 2019).
3. Brash should not be compressed into furrows and drains to slow the flow of water. Instead, brash should ideally be removed from sites and chipped for biomass (also demonstrated by Shah & Nisbet, 2019) or, as a minimum step, prevented from accumulating in areas of preferential flow.
4. This study suggests mulching could be a significant source of soluble carbon and phosphorus, and we suggest that further studies are conducted to assess the environmental risks.
5. Maintaining good records of forest fertiliser applications and other treatments such as liming is recommended to fully understand water chemistry changes with forest-to-bog restoration.
6. Efforts to expand and update tree planting, felling, restoration methods, and high-resolution soil and ground elevation site records for forested areas are recommended.

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Appendices

A1 Supporting information for Chapter 2
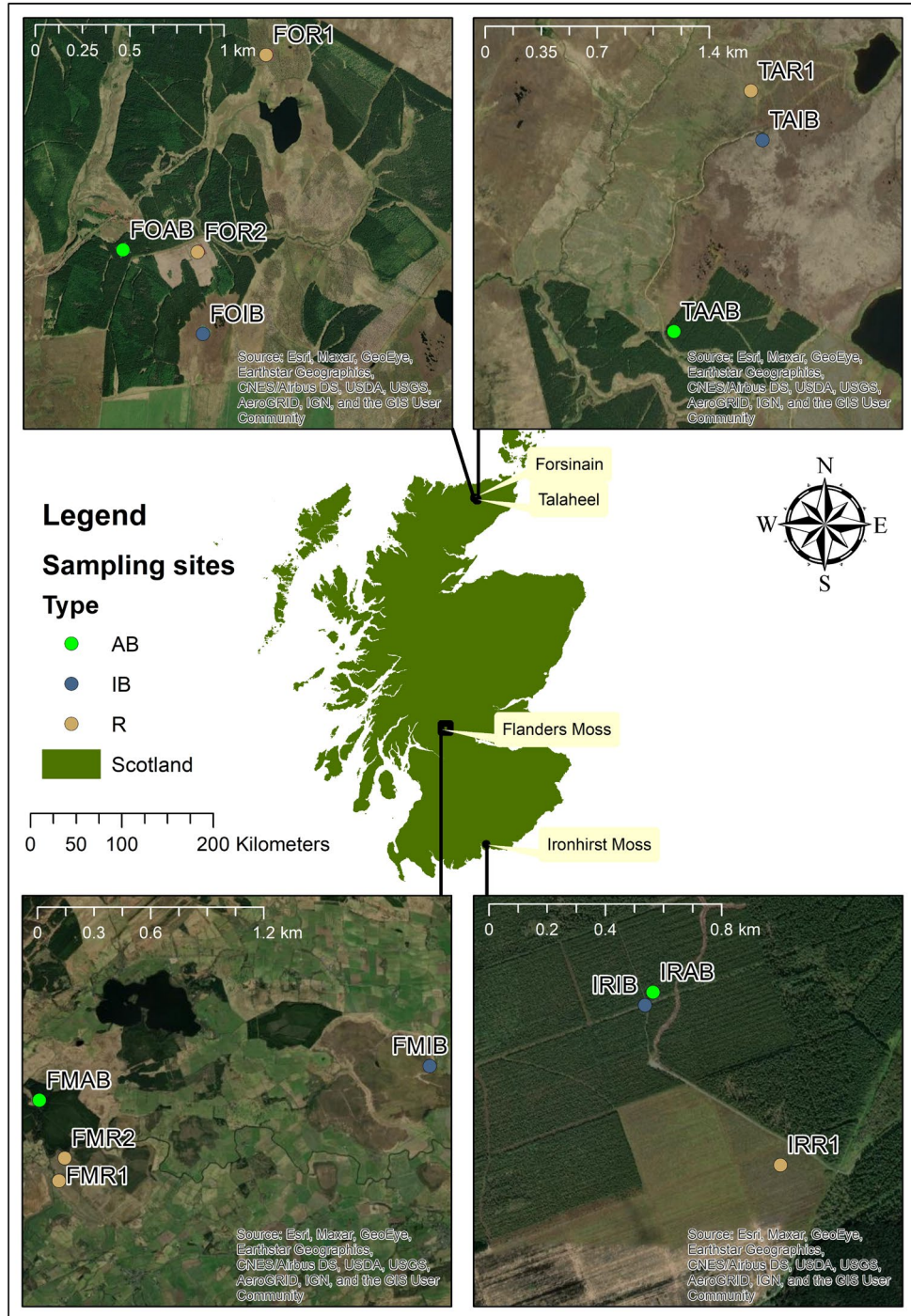
Figure A1-1 – Study site locations – IR = Ironhirst; FM = Flanders Moss; FO = Forsinain; TA = Talaheel; AB = afforested bog; IB = intact bog; R = restored.
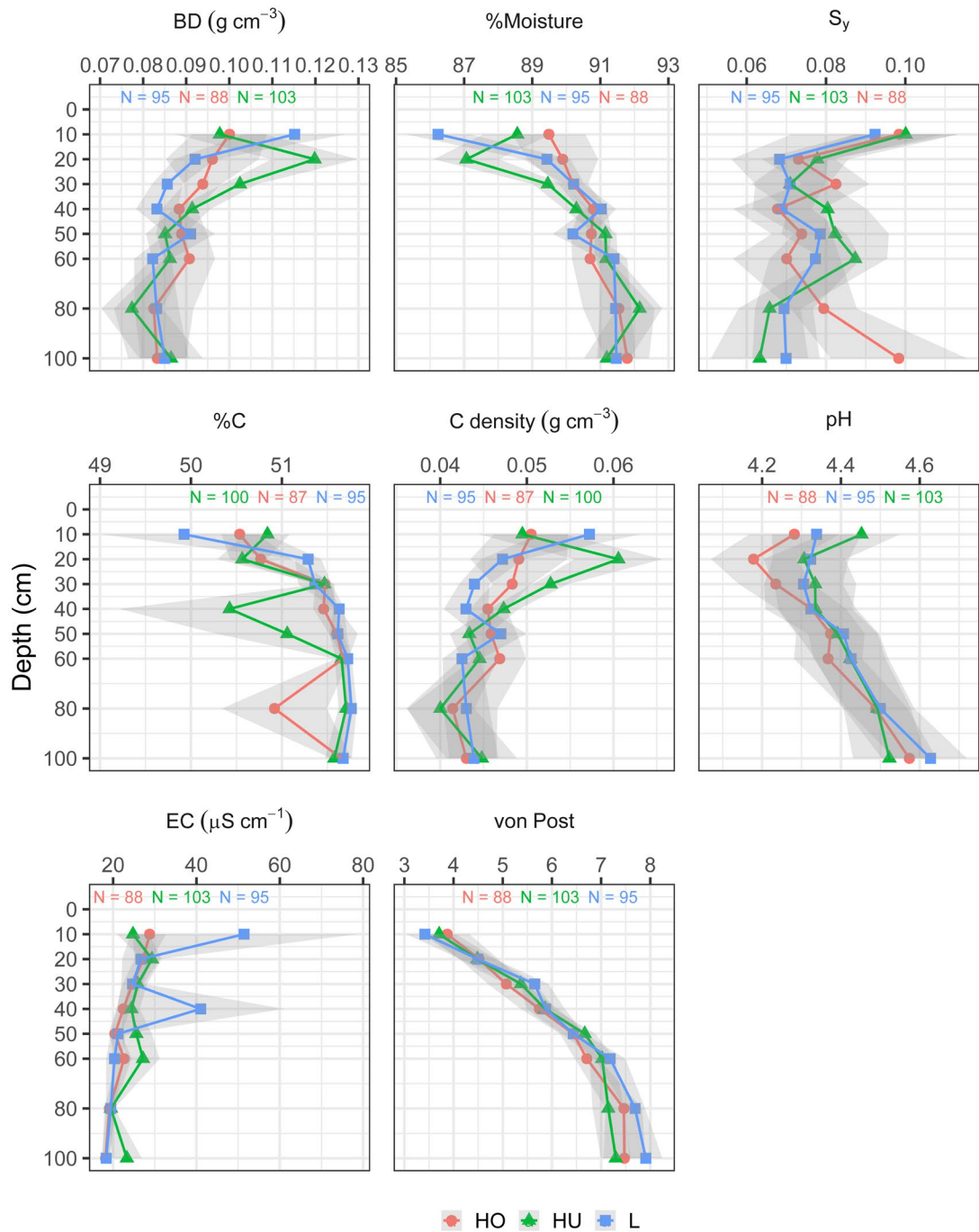
Figure A1-2 – Differences in peat properties intact bog microforms (1 m depth profile) ± standard errors, where HU = hummock, HO = hollow, and L = lawn. BD = bulk density; EC = electrical conductivity. Means were taken for each microform at 10, 20, 30, 40, 50, 60, 80 and 10 cm depths.
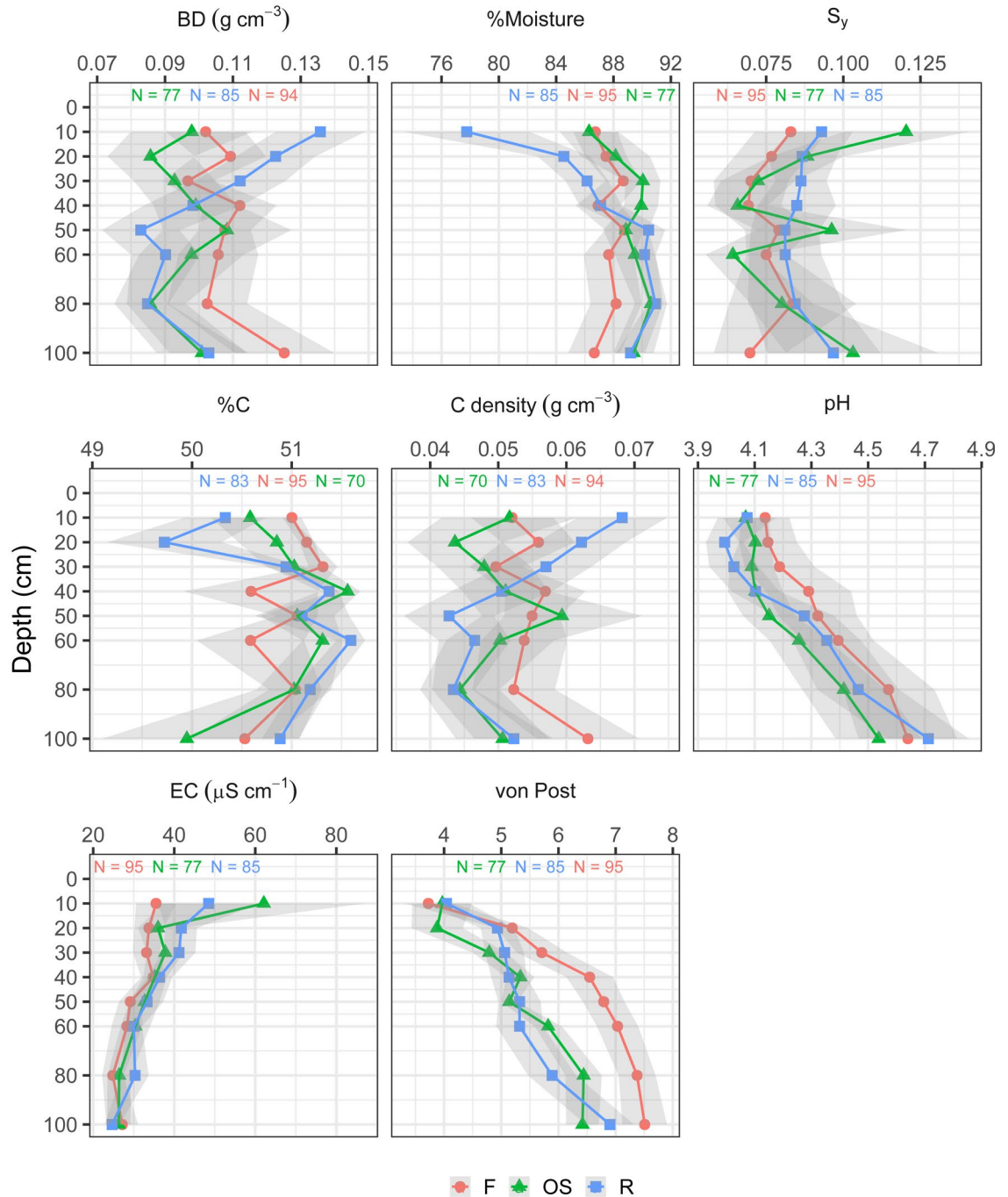
Figure A1-3 – Differences in peat properties for the microforms associated with forestry (1 m depth profile) ± standard errors, where R = ridge, F = furrow, and OS = original surface. BD = bulk density; EC = electrical conductivity. BD = bulk density; EC = electrical conductivity. Means were taken for each microform at 10, 20, 30, 40, 50, 60, 80 and 10 cm depths.
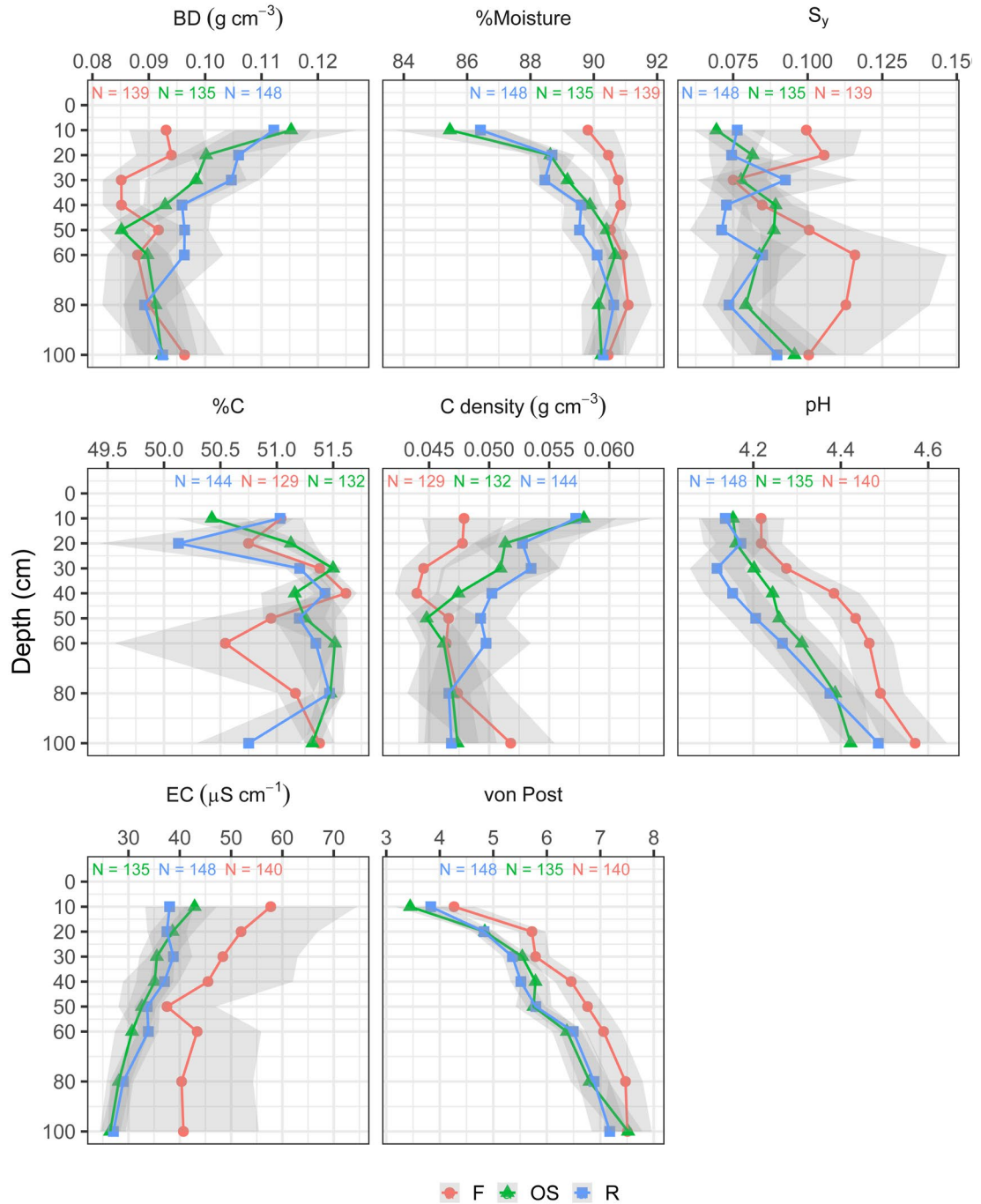
Figure A1-4 – Differences in peat properties for the microforms associated with restoration sites (1 m depth profile) ± standard errors, where R = ridge, F = furrow, and OS = original surface. BD = bulk density; EC = electrical conductivity. Means were taken for each microform at 10, 20, 30, 40, 50, 60, 80 and 10 cm depths.

A2 Supporting information for Chapter 3

A2.1 Tables

Table A2-1 – *Generalised Linear Mixed Model fixed effects for site and sampling month interactions using 'Compound Symmetry' as the covariance type. Subject = unique piezometer identifier; Repeated variable = sampling month.*

| Target	Transformed	Distribution	Link function	F	df1	df2	Sig.
NH$_4$-N	Log	Normal	Identity	13.196	8	971	<0.001
PO$_4$-P	Log	Normal	Identity	13.733	8	958	<0.001
pH	Untransformed	Normal	Identity	13.261	8	1115	<0.001
EC	Log	Normal	Identity	46.072	8	1109	<0.001
DOC	Log	Normal	Identity	10.759	8	1117	<0.001

Table A2-2 – *Porewater chemistry means and standard deviations (SD) for the different afforested and restored surface features (Furrows; Original surface; Ridges), intact bog microforms (Hollows; Hummocks; Lawns) and the land-use type (AB = afforested bog; IB = intact bog; R = restored).*

Type	Microform		DOC (mg L^{-1})	E4:E6	SUVA$_{254}$ (L mg^{-1} m^{-1})	PO$_4$-P (mg L^{-1})	NH$_4$-N (mg L^{-1})	pH	EC (µS cm^{-1})
AB	Furrow	Mean	45.30	6.01	3.82	0.15	1.66	4.30	156
		N	95	73	74	80	80	94	94
		SD	32.68	2.20	0.75	0.18	0.83	0.62	74
	Original	Mean	56.77	5.80	3.58	0.25	1.82	4.30	192
		N	110	87	87	98	98	112	109
		SD	27.72	2.28	0.57	0.26	0.82	0.73	126
	Ridge	Mean	58.74	5.82	3.50	0.34	1.15	3.98	70
		N	34	26	26	31	31	34	34
		SD	15.15	0.99	0.39	0.25	0.64	0.40	15
	Total	Mean	52.49	5.88	3.66	0.23	1.66	4.26	160
		N	239	186	187	209	209	240	237
		SD	28.99	2.11	0.64	0.24	0.83	0.65	105
IB	Hollow	Mean	43.73	9.55	3.63	0.06	0.62	4.29	74
		N	86	61	61	86	86	85	85
		SD	19.34	3.00	0.25	0.23	0.54	0.74	16
	Hummock	Mean	55.08	9.17	3.63	0.05	1.12	4.24	75
		N	116	82	82	82	82	113	113
		SD	24.20	2.52	0.45	0.08	0.63	0.62	22
	Lawn	Mean	48.51	8.71	3.63	0.03	0.92	4.43	77
		N	129	90	90	119	119	128	127
		SD	23.38	3.09	0.51	0.04	0.68	0.74	15
	Total	Mean	49.57	9.09	3.63	0.04	0.89	4.33	76
		N	331	233	233	287	287	326	325
		SD	23.07	2.89	0.43	0.14	0.65	0.70	18
R	Furrow	Mean	64.37	7.50	3.47	0.48	0.84	4.13	101
		N	230	162	162	211	211	227	229
		SD	31.40	2.21	0.31	0.84	1.05	0.53	52
	Original	Mean	62.25	8.81	3.53	0.12	0.57	4.31	89
		N	285	206	212	251	249	288	285
		SD	25.71	3.04	0.48	0.26	1.03	0.79	49
	Ridge	Mean	67.26	8.04	3.40	0.10	0.49	4.10	84
		N	61	39	42	46	46	62	61
		SD	18.63	2.18	0.16	0.24	0.41	0.67	22
	Total	Mean	63.63	8.21	3.49	0.27	0.67	4.22	93
		N	576	407	416	508	506	577	575
		SD	27.53	2.72	0.40	0.60	1.01	0.69	48

A2.2 DOC analysis

The Analytik Jena Multi NC2100 combustion analyser was calibrated from dilutions of commercially prepared organic and inorganic carbon stock standards. Samples were analysed in batches of 20. The calibration and catalyst performance was checked at the start of each batch of samples by measuring Certified Reference Materials (CRMs) and nicotinic acid, respectively. Instrument drift was checked throughout the analysis by measuring a VKI WW4A CRM and check standard (10ppm DOC, 6ppm DIC = 16ppm DC) every 20 samples. A filtration blank was measured in every 20 samples to check for contamination of the filtration equipment. For every 10% of samples, replicates were included to check that the method produced similar values for the same sample. Very few values were above the top standard, and the instrument performs well beyond it. Therefore, no dilution and reanalysis were necessary.

A2.2.1. Commercially prepared stock standards

1000 ppm total inorganic carbon: Merck Life Science UK Limited, 12003-250ML-F

1000 ppm total organic carbon: Merck Life Science UK Limited, 76067-250ML-F

A2.2.2. Certified reference materials

CRM	Organic carbon mg L^{-1}	Inorganic carbon mg L^{-1}
Big Moose-14 (Lot 0120)	4.22 ± 0.49	–
Cranberry-05 (Lot 0918)	3.60 ± 0.51	9.40 ± 0.84
Ontario-12 (Lot 0820)	1.89 ± 0.34	22.00 ± 3.30
VKI WW4A	19.80 ± 0.70	–

A2.3 Auto-analyser colorimetric methods for N and P

Linear calibration of the Skalar San++ colorimetric auto-analyser was performed from 6 equidistant standard stock solutions using pure chemicals. At the start of each batch, the calibration and performance of the instrument were checked by measuring Certified Reference Materials (CRMs). Instrument drift was monitored throughout the analysis by measuring the QC VKI WW1B CRM and the check standard every 35 samples. Drift correction was performed if necessary. Contamination of the filtration equipment was monitored by measuring a filtration blank in each batch of 35 samples. Replicates were produced every 10% of samples to check that the method produced similar values for replicates of the same sample. Values above the top standards of 0.5 mg PO_4-P L^{-1}, 0.5 mg NH_4-N L^{-1}, 0.05 mg NO_2-N L^{-1} and 5 mg NO_3-N L^{-1} were diluted by a factor of 10 and reanalysed.

A2.3.1. Stock standards

NO_2-N, TON, NH_4-N, and PO_4-P stock standards were prepared from pure chemicals.

A2.3.2. Certified reference materials

CRM	NO3-N mg L^{-1}	NH4-N mg L^{-1}	PO4-P mg L^{-1}
VKI WW1B	4.96 ± 0.06	1.00 ± 0.02	0.498 ± 0.06

A2.3.3. Colorimetric NO_2-N analysis

Nitrite was measured at 540 nm from the reddish-purple colour produced when diazonium compounds formed by diazotizing sulphanilamide by nitrite in water under acid conditions are coupled with alpha-naphthyl ethylenediamine dihydrochloride.

A2.3.4. Colorimetric TON analysis

TON (nitrate + nitrite) was measured by reducing nitrate to nitrite by hydrazinium sulphate, and the nitrite (originally present plus reduced nitrate) is determined by the above nitrite method.

A2.3.5. Colorimetric NH$_4$-N analysis

Ammonium was measured at 600 nm from the green coloured complex produced when ammonia is chlorinated to monochloramine, which reacts with salicylate to 5-aminosalicylate.

A2.3.6. Colorimetric PO$_4$-P

Phosphate was measured at 880 nm from the intensely blue complex produced when ammonium molybdate and potassium antimonyl tartrate react in an acidic medium with diluted phosphate solutions to form an antimony-phospho-molybdate complex. The intensely blue complex is formed after it is reduced by ascorbic acid.

A3   Supporting information for Chapter 4

*Table A3-1 – Water balance and mean, maximum and minimum discharge for the eight catchments over the whole study period. Catchment monitoring dates are given. RBAB1 was taken as the afforested bog catchment for Flanders Moss. P = precipitation (mm); Q = total annual discharge (mm); Mean Q = mean discharge (L s^{-1})/(mm d^{-1}); Max Q = maximum discharge (mm d^{-1}); Min Q = minimum discharge (mm d^{-1}) Runoff/rainfall = Q/P (%);AET = actual evapotranspiration P-Q (mm). * - rainfall from the Flanders Moss NNR rain gauge.*
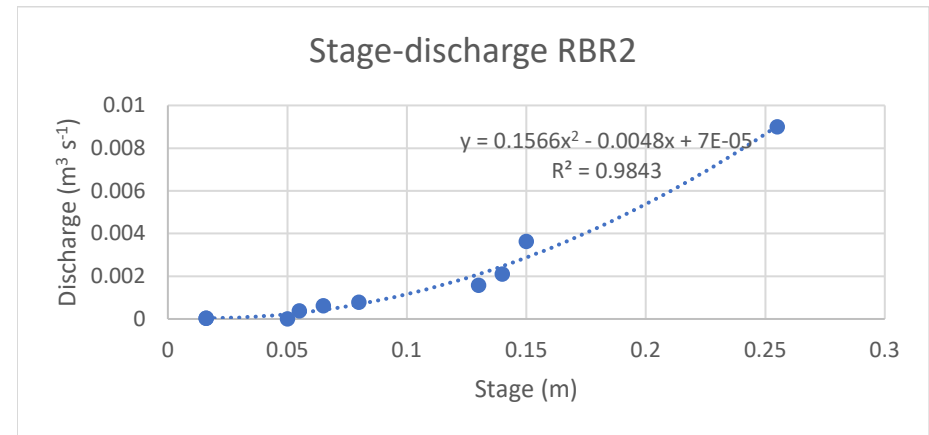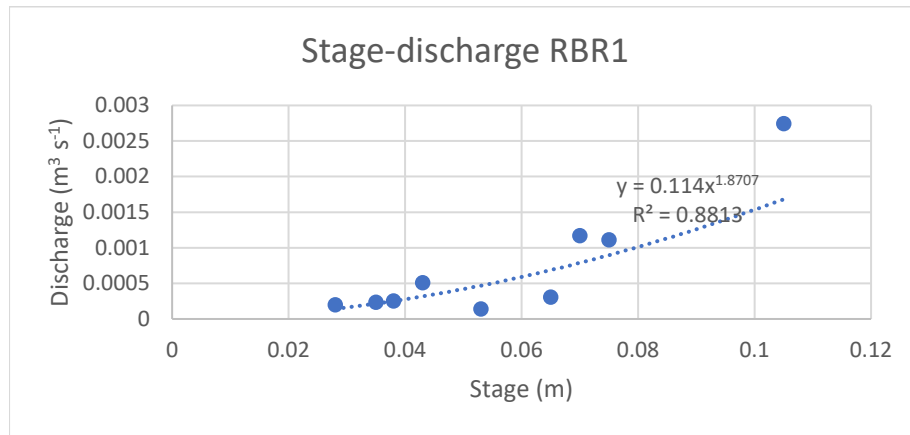
Site	Dates	P (mm)	Q (mm)	Mean Q (L s^{-1})	Mean Q (mm d^{-1})	Max Q (mm d^{-1})	Min Q (mm d^{-1})	Runoff/ Rainfall (%)	AET (mm)
RBIB	27/11/17 - 28/11/19	1942*	1098	1.0	1.5	10.3	0.2	56.5	844
RBAB1	27/03/18 - 30/09/19	1736	598	0.1	1.1	16.8	0.0	34.4	1138
RBR1	26/02/18 - 28/11/19	2030	1020	0.5	1.6	17.2	0.0	50.2	1010
RBR2	26/02/18 - 28/11/19	2030	1149	5.5	1.8	87.9	0.0	56.6	880
BBIB	21/07/18 - 03/11/19	1542	1167	0.4	2.3	35.1	0.0	75.7	374
BBAB	14/06/18 - 03/11/19	1555	872	1.0	1.6	35.5	0.0	56.1	683
BBR1	02/03/18 - 03/11/19	1542	1007	0.4	2.0	35.5	0.0	65.3	534
BBR2	21/07/18 - 03/11/19	1706	1219	0.4	1.5	31.7	0.0	71.5	487

Table A3-2 – Mean storm metrics for the eight streamflow catchments over the whole study period. N = number of storms; Peak Q = peak storm discharge (mm d⁻¹); Peak lag = duration between peak rainfall and peak Q; Recess lag = duration between peak Q and when the quickflow component had returned to zero; Hydrograph Intensity = peak Q divided by (total storm Q x 10^{-6}); BFI – baseflow index; Storm duration = time quickflow > 0 for the storm event. Standard deviations are in parentheses.

Site	N	Catchment area	Peak Q	Peak lag	Recess lag	Hydrograph intensity	BFI	Storm duration
		(ha)	(mm d⁻¹)	(h)	(h)	(s⁻¹)		(h)
RBIB	44	6.01	6.24 (2.00)	14.94 (6.13)	66.16 (53.18)	8.37 (5.08)	0.87 (0.07)	24.59 (12.68)
RBAB1	28	0.67	8.56 (4.16)	15.35 (10.17)	92.68 (45.84)	7.06 (2.54)	0.79 (0.08)	20.87 (12.19)
RBR1	62	2.46	10.00 (2.74)	7.07 (4.66)	57.56 (37.74)	11.65 (3.64)	0.73 (0.08)	17.47 (12.07)
RBR2	73	26.22	12.17 (15.63)	11.10 (8.42)	37.32 (27.72)	19.76 (9.57)	0.59 (0.14)	19.52 (17.30)
BBIB	55	1.64	14.67 (6.91)	6.48 (9.06)	45.56 (38.01)	20.11 (10.11)	0.70 (0.11)	18.29 (14.25)
BBAB	46	5.08	10.08 (5.06)	10.95 (7.88)	69.34 (44.43)	11.18 (5.36)	0.72 (0.10)	22.32 (12.38)
BBR1	61	1.58	11.50 (5.74)	6.61 (7.73)	38.64 (21.37)	19.45 (10.69)	0.68 (0.12)	15.45 (9.64)
BBR2	46	2.27	11.8 (7.54)	10.01 (9.30)	48.42 (30.94)	14.03 (10.36)	0.78 (0.10)	19.91 (14.55)

Table A3-3 – Mean water-table storm metrics for all catchments over the whole study period. WT rise = water-table depth before the storm – Peak WTD; Peak WTD = minimum water-table depth for the storm event; Duration = duration from rainfall start to WT rise for a 0.1 cm rise in the water-table; Peak lag = duration between peak rainfall and peak water-table; 6 h recession rate = difference between peak water-table and 6 hours after the peak divided by 6; 12 h recession = rate difference between peak water-table and 12 hours after the peak divided by 12. Standard deviations are in parentheses.

Site	N	WT rise (cm)	Peak WTD (cm)	Duration (h)	Peak lag (h)	6 h recession rate (cm h^{-1})	12 h recession rate (cm h^{-1})
RBIB	64	2.87 (2.86)	1.87 (3.39)	0.93 (1.01)	9.25 (6.34)	0.11 (0.13)	0.14 (0.17)
RBAB1	35	8.00 (5.62)	12.54 (10.54)	2.18 (2.27)	15.40 (7.49)	0.33 (0.22)	0.44 (0.28)
RBAB2	48	4.44 (4.40)	6.67 (5.46)	1.30 (1.77)	10.39 (5.87)	0.08 (0.05)	0.09 (0.05)
RBR1	78	2.98 (1.98)	3.36 (4.29)	0.69 (0.80)	6.39 (4.38)	0.12 (0.14)	0.13 (0.15)
RBR2	52	3.13 (3.07)	11.00 (6.69)	1.60 (1.78)	10.46 (5.71)	0.09 (0.10)	0.13 (0.17)
BBIB	63	1.98 (2.30)	4.63 (2.72)	0.91 (0.64)	8.96 (6.46)	0.06 (0.12)	0.05 (0.05)
BBAB	39	5.61 (4.78)	15.77 (6.10)	1.13 (1.13)	10.11 (7.00)	0.13 (0.08)	0.15 (0.08)
BBR1	53	2.56 (3.45)	-1.05 (2.86)	1.24 (1.24)	7.74 (6.50)	0.17 (0.22)	0.13 (0.17)
BBR2	61	2.68 (2.63)	3.54 (2.89)	0.87 (0.83)	8.90 (6.42)	0.13 (0.15)	0.13 (0.15)

Stage-discharge RBR1

$y = 0.114x^{1.8707}$
$R^2 = 0.8813$

Stage-discharge RBR2

$y = 0.1566x^2 - 0.0048x + 7E-05$
$R^2 = 0.9843$

RBAB1 used the standard V-notch equation due to site access restrictions:

$$Q = \frac{8}{15} C_d \sqrt{2g} \tan(\theta/2) \left[h_0^{5/2} \right]$$

Where h_0 is the weir head, C_d is the discharge coefficient, g is the gravitational acceleration, and θ is the notch angle in radians.

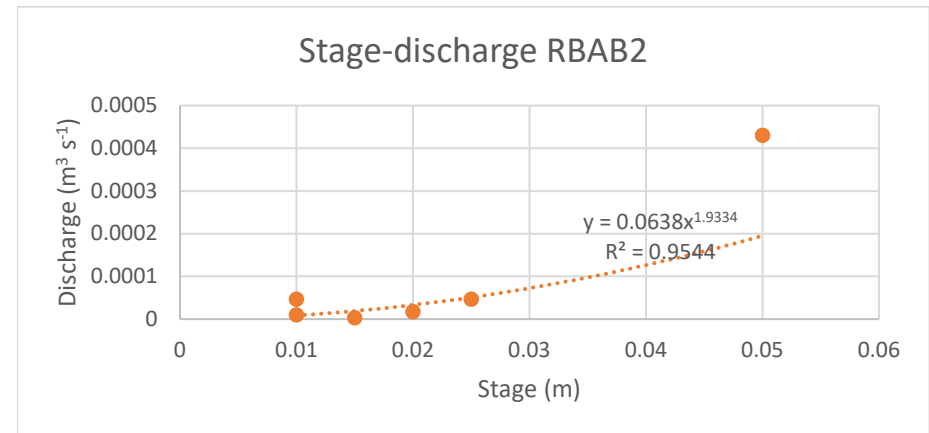Stage-discharge RBAB2

$y = 0.0638x^{1.9334}$
$R^2 = 0.9544$

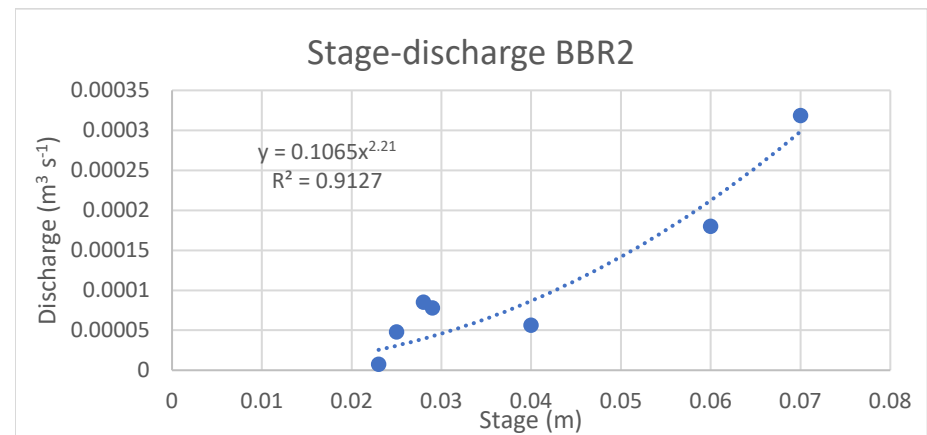*Figure A3-1 – Stage-discharge relationships for the Flanders Moss weirs where applicable.*
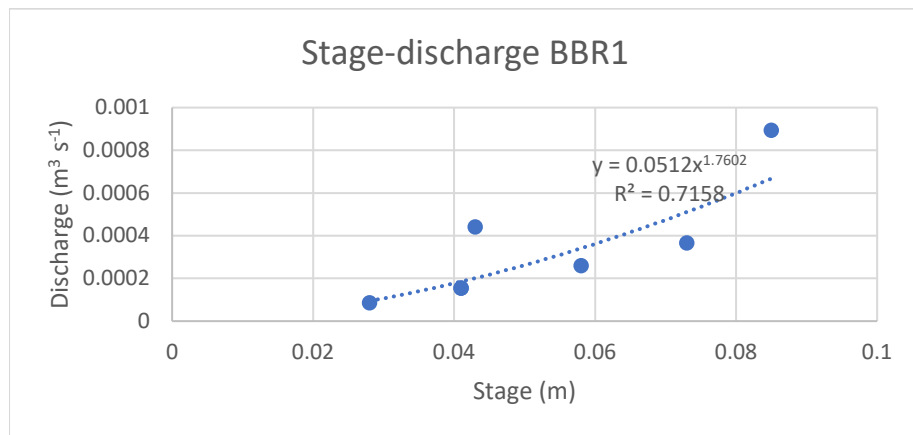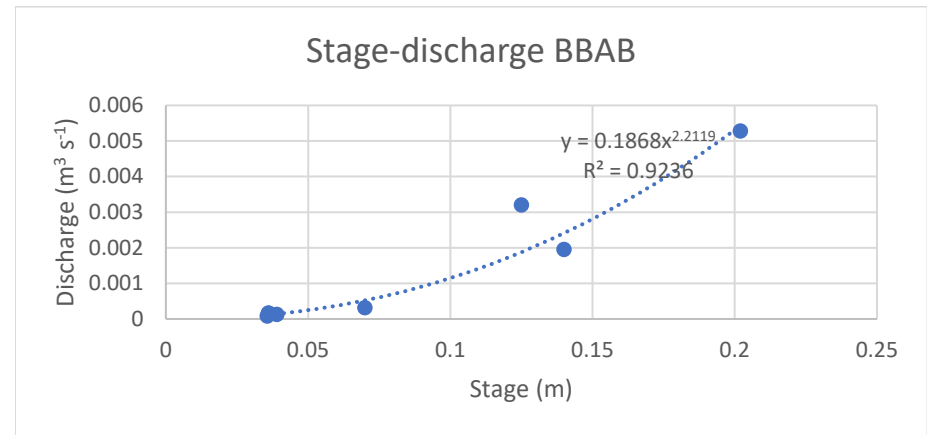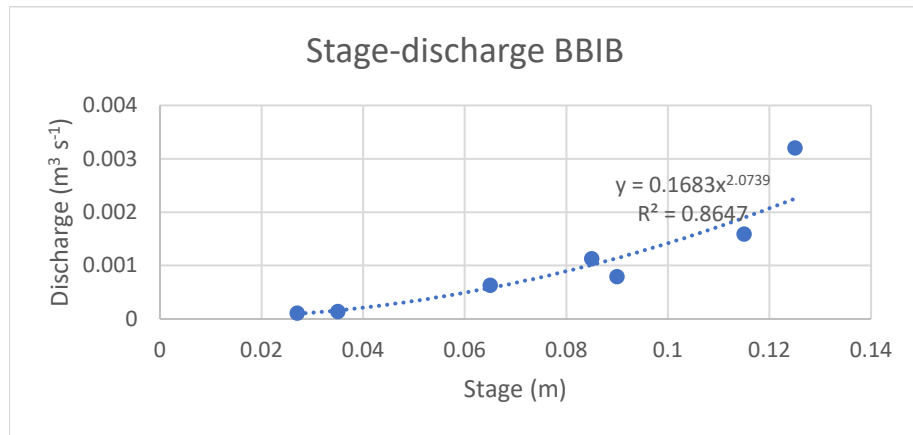
Figure A3-2 – Stage-discharge relationships for the Forsinain weirs.

A4   Supporting information for Chapter 5

The University of Leeds quality control for nutrients and DOC is covered in Appendix A2. The SEPA laboratory quality control was divided into three different types. Not all were used for all methods, depending on whether the analysis method is direct (no preparation or pre-treatment) or if preparation or pre-treatment is involved. Filtration and any preservation chemicals added were performed before instrument analysis. All the primary calibration standards (and independent check standards) were made from ISO Guide 34 traceable materials.

1)   Independent Calibration Check Standards (ICCS) - made up independently from the primary calibration standards, but still separate solutions for each determinand.

2)   Instrument performance check standards (they do not check any preparation or pre-treatment, only the instrument):

- Instrument blank – ultrapure water.
- Instrument performance standards (IPS) – in the case of the auto-analyser and ICP methods, these are mixed standards to check the performance of the instrument over both the high and low ranges

3)   Process checks

- Process Blank – been through all the preparation AND analysis stages.
- Process Check Standards (PCS) – a single standard or mixed standard that has been through the entire preparation AND analysis stages.

The instruments were checked each time they were used, and batches of 20-30 samples were run at a time. Each batch was accompanied by each of the quality assurance/quality control checks. Replicates were not used in the analyses. In addition to these routine checks, SEPA participates in various proficiency testing schemes. All methods go through a validation process to determine Method Detection Limits (MDL's), bias and precision on the full range of matrices the methods cover.

A4.1 Auto-analyser colorimetric methods for N and P

Serial dilution of stock calibration standards was performed internally on the Thermo Scientific Aquakem 600 instrument from the high and low range stock calibration standards.

Determinand	High Range (mg L^{-1})	Low Range (mg L^{-1})
NO$_2$-N	100	10
TON	1000	100
NH$_4$-N	1000	10
PO$_4$-P	100	10

Samples were diluted for two reasons: 1) to reduce the possibility of contamination of the instrument, and 2) to get high samples within the maximum calibration range. Quality control for nutrients auto-analyser: Instrument Blank, Process Blank, ICCS & IPS.

A4.1.1. Calibration standards

NO$_2$-N standards were prepared from solid sodium nitrite.

TON standards were prepared from potassium nitrate.

NH$_4$-N standards were prepared from ammonium sulphate.

PO$_4$-P standards were prepared from solid potassium dihydrogen orthophosphate.

A4.1.2. Colorimetric NO$_2$-N analysis

Nitrite ions react with sulphanilamide to form a diazonium compound which, in dilute phosphoric acid, couples with N-1-naphthylethylene diamine dihydrochloride to form a reddish purple azo dye measured spectrophotometrically at a wavelength of 540 nm.

A4.1.3. Colorimetric TON analysis

TON is determined by measuring the sum of nitrite and nitrate in a sample. Available nitrate is reduced to nitrite by hydrazine under alkaline conditions, using cupric ion as a catalyst. The reduced nitrate, and any nitrite already present, undergo the exact reaction and measurement as the above nitrite test.

A4.1.4. Colorimetric NH_4-N analysis

Ammonia in the sample reacts with 4-hypochlorite ions (oxidant) generated from alkaline hydrolysis of sodium dichloroisocyanurate to form monochloramine. The result reacts with salicylate in the presence of sodium nitroprusside (catalyst) to produce blue indophenol compounds. The colour is measured spectrophotometrically at a wavelength of 660 nm.

A4.1.5. Colorimetric PO_4-P analysis

PO_4-P reacts with ammonium molybdate and antimony potassium tartrate under acid conditions to form a complex. Ascorbic acid reduces the complex to produce an intense blue colour measured spectrophotometrically at a wavelength of 880 nm.

A4.2   ICP – OES analysis of metals

The Perkin Elmer Optima 7300 DV instrument was calibrated from ISO Guide 34 traceable multielement standards.

The calibration ranges are:

- 0-100 mg L^{-1} for Na, K, Ca, and Mg

- 0-40 mg L^{-1} for Fe and Mn

- 0-5000 µg L^{-1} for Al

Samples over range were diluted manually (with calibrated pipettes) and re-run. All samples (and standards) go through the same preparation – filtering (where appropriate), acidification and oven digestion. Quality control for ICP-OES: ICCS, IPS, Process Blank, PCS

A4.2.1. Calibration standards

Primary calibration standards were made from ISO Guide 34 traceable multielement standards. The ICCS for this method was a similar multi-element standard from a different supplier.

A4.3   DOC analysis

The calibration range for the Skalar Formacs^{HT} TOC instrument was $0 – 20$ mg L^{-1}, with the sample range being $0.5 – 20$ mg L^{-1}, where 0.5 mg L^{-1} is the minimum reporting value. Samples over the 20 mg L^{-1} range were diluted and repeated, but only if they were within the time target. If outside time target, they were reported as >20 mg L^{-1}. Quality control for DOC: Instrument Blank, Process Blank, ICCS, IPS & PCS.

A4.3.1. Calibration standards

Calibration standards were made from potassium hydrogen phthalate.