The effects of bog restoration in formerly afforested peatlands on water quality and aquatic carbon fluxes

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The effects of bog restoration in formerly afforested peatlands on water quality and aquatic carbon fluxes

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A thesis presented for the degree of Doctor of Philosophy in Environmental Science at the University of Aberdeen

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Declaration

I, Paul Patrick Joseph Gaffney have composed this thesis. All the work included in this thesis, I have carried out myself with exceptions of Chapter 3 and 4, where set-up and sampling for the peat, needle and brash experiments was carried out by Charlotte Henderson (ERI Intern) and ICP analyses of December and November pore-water samples were carried out by Anne Eberle (ERI Intern). This thesis has received feedback from Roxane Andersen (ERI) my director of studies, and supervisors Mark Taggart (ERI) and Mark Hancock (RSPB), who have helped supervise the design, data analysis and writing of the thesis. All quotations have been distinguished by quotation marks and the sources of information have been specifically acknowledged. This thesis or any part of this thesis has not been accepted in any previous application for a degree.

Paul P.J. Gaffney

31st November 2016
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Abstract

The restoration of drained, afforested blanket bogs (forest-to-bog restoration) is an increasing management practice, due to recognition of both the nature conservation and carbon sequestration services provided by peatlands. Forest-to-bog restoration involves conifer felling (and harvesting) along with blocking of forestry drains. Research from conifer felling and drain blocking on open peatlands shows significant effects on pore- and stream-water quality, when practised separately. However, there is very little knowledge of the combination of both these practices in forest-to-bog restoration.

This research investigated the effects of forest-to-bog restoration on pore-, surface-, stream- and river water quality in the short-term (0-1) years post-restoration, where the effects of restoration are disturbance-related. We also investigated restoration progress across a chronosequence of restoration sites using pore- and surface-water chemistry.

Our results showed significant increases in DOC, phosphate, K and NH$_4^+$ (2-99 fold) in pore- and surface-water in the first year post-restoration, which may have implications for the recovery of bog vegetation. In streams significant increases in Fe (1.5 fold) and phosphate (4.4 fold) were found, with no significant impacts on concentrations in rivers or pass rates for drinking water or WFD standards. We also found no significant effects on aquatic carbon exports. However, as more restoration is carried out within the catchments and the proportion felled increases, greater impacts on streams and rivers may be observed. From our results, we recommend felling small percentages (3-23%) of stream and river catchments and the use of drain blocking and silt traps to retain sediment.

We observed progress in recovery towards bog conditions across a chronosequence of restoration sites (aged 0-17 years); incomplete recovery of WTD and elevated NH$_4^+$ in porewater appeared the main barriers to restoration. Therefore, enhancements such as brash and needle removal and plough furrow blocking may be able to accelerate restoration.
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Glossary and abbreviations

Al: aluminium
AICc: Akaike information criterion (corrected)
ANC: acid neutralising capacity
Ca: calcium
BVOC: biogenic volatile organic compound
C: carbon
CO₂: carbon dioxide
CH₄: methane
CLDs: compact letter descriptors
DIC: dissolved inorganic carbon
DOC: dissolved organic carbon
Fe: iron
FWMC: flow weighted mean concentration
Gt: gigatonnes (10⁹ tonnes)
GHG: greenhouse gas
GLMM: generalised linear mixed model
GLS: generalised least squares
ha: hectares (10 000 m²)
HMW: high molecular weight
LMM: linear mixed model
LOI: loss on ignition
Mg: magnesium
Mn: manganese
Mt: megatonnes (10⁶ tonnes)
Na: sodium
N: nitrogen
Ni: nickel
NH₄⁺: ammonium
P: phosphorus
POC: particulate organic carbon
S: sulphur
SAC: special area of conservation
SNH: Scottish natural heritage
SPA: special protection area
SPM: suspended particulate matter
SUVA: specific ultraviolet absorbance
T: tonne (1000 kg)
TON: total oxidised nitrogen
UK TAG: UK technical advisory group on the water framework directive
WFD: water framework directive
WTD: water table depth
Zn: zinc
1. Introduction

Globally, peatlands are the most common wetland ecosystem (Joosten and Clarke, 2002), defined as land with a naturally accumulated cover of peat (Sjörs, 1980; Bain et al., 2011). They are distributed mainly in high latitudes, with a smaller proportion in the tropics (Yu et al., 2010). When in good condition, peatlands provide a range of ecosystem services to society including biodiversity conservation by habitat provision, water supply and regulation, and climate regulation through sequestration (or capture) of atmospheric carbon dioxide (CO₂) (Chapman et al., 2003; Kimmel and Mander, 2010; Bonn et al., 2016). For instance, boreal and subarctic peatlands cover 3% of the earth’s surface (Limpens et al., 2008; Parish et al., 2008) but account for around one third of the global soil carbon pool in the form of peat (Gorham, 1991), amounting to 560 Gt C (Yu et al., 2010). This is because in peatlands, the inputs of carbon by vegetation through net primary production (photosynthesis) are greater than outputs of decomposition/respiration through gaseous CO₂, methane (CH₄) and aquatic carbon (transport through water) emissions (Gorham, 1991; Waddington and Roulet, 2000; Billett et al., 2010). Over long periods of time, given the large quantities of carbon that they accumulate and store, peatlands have a net cooling effect on the climate (Waddington and Roulet, 2000; Kirpotin et al., 2007). The rate of carbon accumulation in boreal peatlands (Europe, Russia and North America) was calculated to average 23 t C km⁻² yr⁻¹ (Gorham, 1991; Loisel et al., 2014). If through degradation, the balance shifts from greater net primary production to greater respiration, peatlands become net carbon sources to the atmosphere, fuelling climate change (Moore et al., 1998; Rowson et al., 2010). Therefore, halting the net loss of carbon from terrestrial stores like peatlands is important to help mitigate anthropogenic climate change (Worrall et al., 2011; Artz et al., 2014; Blain et al., 2014; European Commission, 2016a).
1.1 Peatland carbon cycle

The peatland carbon cycle (Figure 1.1) is a balance between inputs and outputs of gaseous and aquatic forms of carbon of which CO$_2$ is often the largest single component (Roulet et al., 2007; Billett et al., 2010; Dinsmore et al., 2010). Through photosynthesis, plants use atmospheric CO$_2$ to build biomass (Clymo and Reddaway, 1971; Loisel et al., 2012). Some of this carbon is emitted back to the atmosphere through aerobic respiration, where plants re-convert carbohydrate into CO$_2$ and carbon is also emitted back through decomposition by micro-organisms (Verhoeven and Toth, 1995; Frolking et al., 1998; Tuittila et al., 2004). When vegetation dies, it begins to undergo microbial decomposition in the aerobic layer where the end product is CO$_2$. This process is much slower under (regularly) water saturated conditions due to a lack of oxygen, therefore organic matter begins to form peat and CO$_2$ release is reduced (Gorham, 1953; Clymo, 1984). When plant remains become more deeply buried over time, decomposition is further retarded because of permanent waterlogging (Moore and Knowles, 1989). Under anaerobic conditions, CH$_4$ is the by-product of decomposition by archaea (Moore and Knowles, 1989). Once produced, methane can be oxidised back to CO$_2$ as it travels through the oxidative layers (Cicerone and Oremland, 1988; Segers, 1998), or can by-pass the aerobic layers and be emitted directly to the atmosphere. Classically peatlands comprise a partially aerated upper later (acrotelm; decomposition by fungi and bacteria) and a deeper permanently saturated layer (catotelm; anaerobic decomposition), where peat formation occurs (Ingram, 1978; Holden and Burt, 2003a; Thor mann, 2006). However, in reality peatland structure is more complex than a two-layer model, and the term “mesotelm” has been used to describe the biogeochemical layer at the interface, within which water table fluctuates (Clymo and Bryant, 2008; Morris et al., 2011).

Carbon is also released from peatlands as biogenic volatile organic compounds (BVOCs) which are products of normal metabolic functioning of vegetation as well as decomposition processes (Laothawornkitkul et al., 2009; Faubert et al., 2011). Together CO$_2$, CH$_4$ and BVOCs are the main carbon-derived gaseous outputs from peatlands. Although not carbon based, nitrous oxide is a greenhouse gas (GHG) gas also emitted from peatlands, which is part of the peatland GHG budget (Alm et al., 1999; Roulet, 2000).
Figure 1.1: Schematic of simplified peatland carbon cycle, showing the inputs and outputs. Living vegetation (in green) takes up CO₂ from the atmosphere. Some is emitted back through plant respiration and then through decomposition by fungi in the aerated layer when plants die. All pathways of CO₂ are shown in black. When plant remains become deeply buried reaching the waterlogged layers, anaerobic decomposition by archaea produces CH₄ (CH₄ pathways are shown in red). As CH₄ passes through the aerated layer to the atmosphere, some is oxidised to CO₂. DOC is the soluble product of organic matter decomposition in porewater and is flushed out to streams by water movement. A small contribution to DOC can be made from (live) plant root exudates. Additionally, surface runoff passing over the peatland surface accumulates DOC (All DOC pathways are shown in blue). BVOCs are a smaller component of the peatland carbon cycle produced both from decomposition and plant metabolism (BVOC pathways in green). Water table movements, which often show a seasonal pattern, strongly influence decomposition processes. In a pristine peatland acting as a net carbon sink, the inputs of carbon through photosynthesis are greater than the combined outputs.
The main aquatic carbon component is dissolved organic carbon (DOC) which is the soluble product of organic matter decomposition (Moore, 1997). It comprises of a range of molecules of varying size and complexity from simple amino acids and carbohydrates to complex humic substances (Robards et al., 1994). DOC accumulates in peat porewater and is flushed out by water movement to streams (Fraser et al., 2001; Billett et al., 2006). Additionally, DOC is released to surface runoff water as it interacts with vegetation and the surface peat (Proctor, 2006). There is also a very small input of DOC (e.g. 1-2 mg L\(^{-1}\)) to the peatland through precipitation (Moore, 1997). Further to this, other components of aquatic carbon, are dissolved inorganic carbon (DIC), particulate organic carbon (POC) and dissolved CO\(_2\) and CH\(_4\), found in much smaller proportions (Dinsmore et al., 2010, 2013; Chapter 5; Figure 5.1). Thus, aquatic carbon export from a peatland, depends primarily on the concentration of DOC in porewater, and on the rate at which water flows out of a given peatland.

1.2 Peatland classification
Northern peatlands are broadly classified as bogs or fens. Bogs are ombrotrophic, i.e. rain-fed peatlands (Aerts et al., 1999), receiving nutrients only from precipitation. Bogs tend to be more acidic than fens with pH typically less than 4.2 (Glaser, 1992). Fens are minerotrophic peatlands i.e. they receive nutrients from precipitation, surface water and groundwater (Aerts et al., 1999). Bogs and fens support different vegetation (Forrest and Smith, 1975; Chee and Vitt, 1989). This is reflected in the composition of the peat; bog peat mainly comprises remains of bryophytes, while both vascular plants and bryophytes are found in fen peat (Graf and Rochefort, 2009).

In the British Isles, bogs are the dominant peatland, and are found either as raised bogs or blanket bogs (Lindsay et al., 1988). Raised bogs typically occur as isolated dome shaped units of ombrotrophic peat in a wider landscape not dominated by peat bogs (Lindsay, 1995). Blanket bogs are not confined to basins instead covering a landscape (except the steepest slopes) with waterlogged peat favouring Sphagnum growth (Moore, 2002). Within the British Isles, blanket bogs are present mainly in the upland areas of western and northern Scotland and western Ireland (Lindsay, 1995; NPWS, 2015). However, there can be fen intrusions in blanket bog dominated landscapes, in nutrient
rich areas, e.g. where there are streams with a mineral input. Therefore, fens and bogs can, and often do form mosaics within the same landscape (Waughman, 1980).

In Europe, there are several designations, i.e. legal forms of protection, under European Commission directives on blanket bog peatlands, both as an important habitat (Special Area of Conservation (SAC): EU Habitats Directive, 92/43/EEC; EC, 2007) and for their characteristic bird communities (Special Protection Area (SPA): EU Birds Directive; EC, 2009). This protection follows earlier protection under UK legislation (Sites of Special Scientific Interest (SSSI): 1981 Wildlife and Countryside Act; UK GOV., 1981), which ultimately helped limit the scope of forestry planting in the 1980s on UK blanket peatlands. The degree of conservation protection given to bogs means that they are high value habitats and are in some cases managed to a strong conservation agenda e.g. (Holden et al., 2008; Wilson et al., 2014; Sozanska-Stanton et al., 2016). On a national scale, UK peatlands (>45 cm depth) are estimated to cover 21 120 km$^2$, with the majority of this in Scotland (82%; Cannell et al., 1993). More recently, all peat deposits in Scotland were estimated to cover 17 270 km$^2$, (22% of land area) and store 1620 Mt of carbon, with the majority (64%) of Scottish peat found as blanket bog (Figure 1.2; Chapman et al., 2009).

Covering 4000 km$^2$, the Flow Country peatlands of Caithness and Sutherland are the single most important area of near-natural blanket bog in the UK (SNH, 2005) and is the UK’s single largest soil carbon store (Milne and Brown, 1997; Chapman et al., 2009). The Flow Country peatlands are of exceptional conservation importance (Lindsay et al., 1988), with many designated SAC sites for pristine blanket bog habitat and associated water bodies, and designated SPAs for its populations of breeding waders and ducks (Stroud et al., 1987). Additionally, the Flow Country peatlands are the source of many rivers which support Atlantic Salmon (Salmo salar) populations (Youngson et al., 2002).
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1.3 Blanket bog management and impacts
The management and exploitation of peatlands has been carried out globally, where there are many unsustainable practices occurring, despite various degrees of protection by national and international conservation agreements (Joosten et al., 2012). It is estimated that 1.8 M ha out of a total of 2.3 M ha of UK peatlands have been damaged in some way (Bain et al., 2011). In Scotland alone, it was estimated that 1 M ha could benefit from some degree of restoration, out of which 350 000 ha are severely damaged (Artz et al., 2012).

In UK blanket bogs management ranges from drainage to improve grazing or agricultural use (Wilson et al., 2011c), managed burning (Clay et al., 2012; Ramchunder et al., 2013), peat extraction for fuel (Cooper et al., 2001) and drainage for planting with commercial
forestry (Cannell et al., 1993, 1999; Hargreaves et al., 2003). Peatland drainage for commercial forestry has been a common practice across the globe, with plantations in North America, Finland, Germany, Ireland and the UK (Sjörs, 1980; Cannell et al., 1993; Landry and Rochefort, 2012; Hommeltenberg et al., 2014; Renou-Wilson and Byrne, 2015). In the UK, these areas were drained by ploughing deep ditches, after which they were commonly planted with a mixture of non-native Sitka spruce (Picea sitchensis) and Lodgepole pine (Pinus contorta) species (Stroud et al., 1987; Forestry Commission Scotland, 2015; Anderson et al., 2016). As drainage and afforestation contribute to a lower water table and loss of peat forming vegetation on the surface (Holden et al., 2004), they impact on carbon sequestration (Hargreaves et al., 2003; Rowson et al., 2010) and peatland water quality (Lundin and Bergquist, 1990; Wilson et al., 2011a).

1.3.1 Blanket bog restoration

The recognition of the negative effects of management practices such as drainage and afforestation on blanket bog habitat and functions (Cannell et al., 1993; Holden et al., 2004; Hancock et al., 2009; Forestry Commission Scotland, 2015) led to a shift in peatland management towards restoration of degraded or damaged blanket bog (Lunt et al., 2010; Bain et al., 2011; Parry et al., 2014). The key aim of blanket bog restoration is to restore the water table and hydrological regime to its natural state and promote re-establishment of peat forming vegetation (Holden et al., 2007b; Lunt et al., 2010; Wilson et al., 2010; Bellamy et al., 2012; Parry et al., 2014). In achieving this, restoration of other peatland functions (carbon sequestration, nutrient cycling, flood regulation, nature conservation) may also follow (Lunt et al., 2010; Joosten et al., 2012; Bonn et al., 2016).

Early blanket bog restoration was driven by conservation of the habitat to protect specialist vegetation, e.g. conserving areas with high Sphagnum cover (Lindsay et al., 1988), or to protect internationally important populations of breeding waders (Stroud et al., 1987). For example, the numbers of greenshank, dunlin and golden plover on the Caithness and Sutherland Flow Country peatlands, declined significantly as they were displaced by afforestation, with additional impacts on bogs adjoining forestry (Hancock et al., 2009; Wilson et al., 2014). Their conservation remains a significant driver in current restoration of these afforested peatlands. More recently, the recognition of the importance of peatlands in the global carbon cycle has added considerable weight to the blanket bog
restoration effort, and set natural carbon storage higher on the political agenda (Lunt et al., 2010). A UK study found that in 62% of 145 peatland restoration projects in the UK, carbon storage was used as a clear justification, albeit not the main priority (Holden et al., 2008). In 2011, a target of restoring 1 M ha by 2020 in the UK was proposed as a means to achieve 1% of the annual GHG emission reductions, in the UK 2027 emissions targets (2.5 Mt CO$_2$ Eq. yr$^{-1}$; Bain et al., 2011), while the abatement potential from restoring 1 M ha in Scotland could range from 0.5 – 4.8 Mt CO$_2$ Eq. yr$^{-1}$ (Artz et al., 2012). In Scotland, this has been a major factor in the current drive for peatland restoration, which led to a £15 million investment in peatland restoration by the Scottish Government in 2013 (The Scottish Government, 2013).

1.3.2 Restoration of afforested blanket bog
The restoration of afforested blanket bog, hereafter termed forest-to-bog restoration involves the removal of trees, either by felling to waste, harvesting or mulching (Hancock et al., 2014; Muller et al., 2015; Anderson et al., 2016). This is accompanied by blocking of the main forestry drains, although plough furrows (smaller ditches between which trees were originally planted) can also be blocked to further enhance water retention (Anderson, 2010). The restoration of afforested peatlands is already carried out by various organisations including nature conservation organisations (RSPB; Hancock et al., 2014), wind farm developers (Scottish Power Renewables, 2015) and the Forestry Commission (Anderson, 2010). As a result, substantial areas of afforested blanket bog in the UK have undergone forest-to-bog restoration (at a rate of around 500 ha per year, since 2000; Anderson et al., 2016), where trees have been felled or harvested and forestry drains blocked.

Methods of forest-to-bog restoration are evolving over time. The method of tree removal is related to the size of the trees and value of the timber (Anderson, 2010). Initial work in the Flow Country of Caithness and Sutherland in Northern Scotland (Forsinard Flows National Nature Reserve), involved manual “felling to waste” using chainsaws, as the trees were small (Hancock et al., in prep.). Following that older trees were then felled to waste into the furrows using machinery, and the main collector drains were blocked (Andersen et al., 2016). However, this method became less viable, over time as older (and larger) trees did not fit into furrows. Recently enhancements have been carried out on
these sites whereby trees were machine crushed into the plough furrows to create a flatter surface across the restoration area. Original methods of fell-to-waste therefore leave a substantial source of nutrients on site (Anderson et al., 2016), which may be released to watercourses (Neal and Reynolds, 1998; Cummins and Farrell, 2003a; Asam et al., 2014b; O’Driscoll et al., 2014b). Larger trees led to the use of harvesting using specialist low ground pressure machinery (Andersen et al., 2016) and this also offered potential for cost savings through timber income. Harvesting involves tree felling and then removing the stems and leaving brash (tree tops and branches; FC, 2011) on site, or, in other cases removing brash material too; whole tree harvest (Kiikkilä et al., 2014). Additionally, mulching of whole trees has been practiced, where it is not economically favourable to harvest smaller trees (Andersen et al., 2016). Mulch may decompose faster, speeding up restoration (Muller et al., 2015) but cause more risk to water quality. Drain blocking has also evolved from the use of plastic piling, to using peat dams in some cases, e.g. taking peat from the plough furrows created when trees were planted, as an economical and effective method of retaining water (Armstrong et al., 2009; Parry et al., 2014).

Forest-to-bog restoration sites generally retain the microtopographical features created during forest establishment (such as ploughed furrows and plough-throws/ridges), after restoration (Hancock et al., in prep.). Over time, with successful restoration furrows fill with water and become re-vegetated (ideally with Sphagnum mosses) and more recent restoration methods have sought to create a flatter peat surface (by flattening plough throws: (Scottish Power Renewables, 2015). In more recently restored sites, in addition to main collector drains, some plough furrows have also been blocked with peat dams, to increase the effectiveness of re-wetting. Furrow blocking has been found to enhance water table depth (WTD) and bog vegetation recovery in the first five years post-restoration (Anderson, 2010). However, an important question remains to determine the best method of forest-to-bog restoration for long term recovery to bog and also financial cost, as cost-effective restoration may allow larger areas to be restored.

Currently UK forestry policy, prevents any new planting on deep peat (>50 cm; Forestry Commission Scotland, 2015). It also states that afforested areas on deep peat which are reaching harvestable age, may not undergo a second rotation if substantial modifications are required e.g. fertilisation or further ground preparations (Forestry Commission Scotland, 2015). Given that in Scotland 150 000 ha of deep peat (>50 cm) and 590 000
ha of shallow peat (<50 cm) are afforested (Morison et al., 2010) there is a large potential for significant forest-to-bog restoration, where second forestry rotations may not be economic or suitable (Morison, 2013). Documenting some of the impacts of this fast paced land-use change is the focus of the present research.

1.4 Afforestation and restoration of blanket bogs: impacts on ecosystem functions and services in the UK context

1.4.1 Peatlands and water regulation
As areas with a positive water balance, the water table depth (WTD) in pristine blanket bog is near to the surface and the peat is saturated (Holden et al., 2011; Wallage and Holden, 2011). Therefore, blanket bogs store large quantities of water and comprise the headwaters of many major rivers in the UK, thus playing an important role in flood regulation (C. Evans et al., 1999; Bullock and Acreman, 2003; Holden and Burt, 2003b). Blanket bog drainage (to improve livestock grazing) has been found to both increase and decrease the sensitivity of catchments to storm runoff (Conway and Millar, 1960; Burke, 1967) although this depended upon vegetation cover, peat decomposition, drain spacing and effect on water storage (McDonald, 1973; Robinson, 1985). In the longer-term drainage can cause decomposition and subsidence, which acts to increase the speed at which water can escape from the catchment, giving higher peak flows (Holden et al., 2004). In more recent years, blanket bog restoration (by drain blocking) which aims to raise the water table may reverse these changes by reducing peak flow response (Wilson et al., 2011b). However, surface roughness may be a more important factor than drain blocks in determining peak flows and flashiness in streams (Ballard et al., 2012; Lane and Milledge, 2013).

In some areas of the UK (e.g. Yorkshire) blanket bog catchments are an important supply of drinking water (Murray et al., 2007; Worrall et al., 2007). In order to comply with EU water directives, drinking water from peaty catchments has to be decoloured, and the dissolved organic carbon (DOC; Murray et al., 2007) has to be removed. Toxic bi-products can form during the regular drinking water treatment (Bull et al., 1995; Hsu et al., 2001), which in turn are costly to remove. Therefore, management activities such as drainage which increase blanket bog DOC concentrations and therefore colour, are of
concern to the water industry but restoration which can reduce DOC in the longer-term, may be a solution (Wallage et al., 2006; Ritson et al., 2014).

In other areas of the UK the high water quality of peatland rivers support populations of Atlantic Salmon (*Salmo salar*; Youngson et al., 2002). In the Flow Country, there are several (SAC designated) salmon fishing rivers draining blanket bog catchments, supporting a salmon fishing industry, which is a vital element of the Highland’s economy (Butler et al., 2009; Mainstone et al., 2012). Whilst being sourced from a low nutrient environment, rivers draining blanket bogs are rich in DOC-metal complexes which transport metals in soluble or colloidal (in suspension) form to coastal waters (Batchelli et al., 2010; Krachler et al., 2010). This mechanism reduces metals toxicity compared to the free metal ion. For instance, DOC-Al complexes are significantly less toxic than free Al to Atlantic salmon (Gerhardt, 1993; Kroglund et al., 1999).

Practices such as blanket bog afforestation and subsequent felling can disrupt biogeochemical cycles and affect water quality, by increasing concentrations of DOC and metals such as Al (Cummins and Farrell, 2003a; Harrison et al., 2014; Muller et al., 2015). Several studies of peatland forestry felling have shown that there can be significant stream water increases in nitrate, phosphate and potassium (>4 fold), which have taken up to four years to recover (Cummins and Farrell, 2003a, 2003b; Rodgers et al., 2010; Asam et al., 2014b; Finnegan et al., 2014b). Even though peatland restoration may lead to better water quality in the long-run, it is initially a disturbance. Thus, it is essential to understand how it impacts on sensitive connected ecosystems such as freshwater streams and rivers because of the potential ecological and economic impacts (Webster et al., 1992; Wallace et al., 1997; Martin-Ortega et al., 2014), but also because of the need to comply with the mandatory EU Water Framework Directive (WFD) standards (O’Driscoll et al., 2013). This research will document for the first time the short- (0-1 year; chapters 3, 4, 5) and long-term impact (0-17 years; chapter 6) of standard and novel techniques combining tree removal and drain blocking for forest-to-bog restoration.
1.4.2 Peatlands and climate regulation

One of the most widespread blanket bog management interventions, is restoration of drained open blanket bog sites by drain or ditch blocking (Holden and Armstrong, 2007; Armstrong et al., 2009). This acts to slow the flow of water leaving a catchment and to better retain that water, thus allowing the WTD to increase and the peat to re-wet (Holden et al., 2004). Artificial dams are constructed at intervals along existing drains (Armstrong et al., 2010) often using Perspex or peat (as in the Flow Country) or heather bails (Holden et al., 2004) or a variety of other materials, including wood (Parry et al., 2014). As a result of increased interest in peatland carbon dynamics there have now been numerous studies that have focussed on the effects of drain blocking on hydrology and aquatic carbon in open bog sites (Armstrong et al., 2010; Wilson et al., 2011a). These studies have generally found reduced aquatic carbon losses following restoration (Gibson et al., 2009; Parry et al., 2014). Restoration of open blanket bog has been found to benefit water quality, reducing colour and DOC concentrations in the short-medium term (1-3 years; Wilson et al., 2011a) as well as reductions in suspended sediment loads (Parry et al., 2014). It also promotes re-vegetation with Sphagnum, the main peat forming vegetation in bogs (Peacock et al., 2013) and recent work as shown benefits on reduced gaseous carbon emissions (Komulainen and Tuittila, 1999; Waddington et al., 2010). However, in the short term, restoration may be more of a disturbance, causing large increases in pore water concentrations of DOC and metals (Fenner et al., 2001, 2011), which may be closely related to the success of vegetation recovery (Bragazza et al., 2012b).

One of the most pertinent issues surrounding the peatland carbon cycle, is that of the impact of drainage and afforestation of blanket bogs with conifers (Byrne and Farrell, 2005; Renou-Wilson and Byrne, 2015). While naturally forested bogs are able to function as long term net carbon sinks from both trees and understory bog vegetation inputs (Hommeltenberg et al., 2014), the situation in drained and afforested blanket bogs of the UK and Ireland is quite different. Drainage first lowers the water table, leading to loss of wet vegetation and oxidation of the upper peat layers as it dries out (Holden et al., 2004). This can be followed by complete loss of understory bog vegetation as the forest canopy develops (Renou-Wilson and Byrne, 2015). The resulting situation is that trees continue to sequester carbon while the bog does not, although this is complicated slightly by the inputs from litterfall (Byrne and Farrell, 2005). The effect of plantation forestry on the net carbon balance has not been measured at the scale where it can be confidently
determined (Renou-Wilson and Byrne, 2015). However, smaller scale measurements and modelling suggest that in the short term afforested peatlands may be a sink of carbon but only while the trees are photosynthesising (Cannell et al., 1993; Hargreaves et al., 2003). In the longer term, losses of soil carbon may outweigh gains made by trees (Anderson et al., 2016).

At the end of a rotation, harvesting can cause significant physical disturbance (Nugent et al., 2003) as well as disturbance to the biogeochemical cycling (Cummins and Farrell, 2003a; Finnegan et al., 2014b), with direct impacts on gaseous and aquatic carbon cycling (Gordon et al., 1987; Huttunen et al., 2003; Nieminen, 2004). The scope for second forestry rotations on blanket bog is decreasing given that the trees often grow poorly, significant preparation may be required for the second rotation (fertilising, ploughing, planting) and the general policy direction in the UK that forestry on deep peat is not advised (Morison, 2013; Forestry Commission Scotland, 2015).

Therefore, restoration of afforested blanket bogs (forest-to-bog restoration) is an obvious solution for afforested sites (Anderson et al., 2016), given the Scottish Government policy and investment in restoration (SNH, 2015). As restoration is in part driven by carbon savings, the effects of this management on the carbon cycle is a pressing research question. This knowledge could help drive further policy developments in the management of afforested deep peat, as there are also areas still currently intended for replanting. A recent study found that 15+ years after restoration, a previously afforested blanket site was functioning as a net carbon sink, but displayed higher rates of both net primary production and respiration when compared with an open near-natural blanket bog (Hambley, 2016). Further work is in progress to measure the short-term GHG changes associated with the initial disturbance (Hermans et al., 2014). However, any peatland carbon budget is incomplete without measuring aquatic carbon loss, especially given that aquatic carbon can be 25-50% of carbon loss from blanket bogs (Dinsmore et al., 2010, 2013). Moreover, tree felling and drain blocking (on open bog) have both separately shown to affect DOC concentrations and stream flows (Gibson et al., 2009; Wilson et al., 2011a; Ryder et al., 2014). So far, no studies have looked at the initial impact of the combination of tree removal and drain blocking on DOC when evaluating forest-to-bog management. This is an important knowledge gap which this research aims to fill (Chapter 5).
1.4.3 Nutrient cycling

In the short term, the disturbances associated with forest-to-bog restoration could also disrupt nutrient cycling within the ecosystem. This is firstly a physical disturbance as tree removal involves the use of large machinery driving on the peat surface. Secondly, the process either leaves trees on site or brash or mulch are left behind, which decompose over time and release nutrients (Palviainen et al., 2004a; Asam et al., 2014b). Thirdly, there is a cessation of nutrient uptake by trees, which contributes to the increasing nutrient levels (Rosén et al., 1996). Finally, the combination of reduced rainfall interception by trees (Nisbet, 2005) and drain blocking, raises the water table which in itself stimulates decomposition processes within the peat matrix (Fenner et al., 2011). Therefore, forest-to-bog restoration has the potential to dramatically alter surface and pore water chemistry in situ.

There are few studies on the short term response to felling on blanket bog in porewater; these have found increased nutrient concentrations (Asam et al., 2014b; Finnegan et al., 2014a). As shown in the previous section, the effects of drain blocking on DOC in pore and surface water is well researched (Wallage et al., 2006; Gibson et al., 2009; Armstrong et al., 2010); however, there is a distinct lack of knowledge of its effects on other water quality variables. Although these significant effects on porewater (nutrients and DOC) from felling or drain blocking are known when practised separately, the combination of felling and drain blocking as seen in forest-to-bog restoration is novel with respect to effects on surface and pore water quality (Chapter 3).

The time required for successful peatland restoration to occur is generally not well-known, with various studies having found restoration sites approaching the functionality of natural reference sites but without complete recovery (Andersen et al., 2010, 2013b; Haapalehto et al., 2011). While there is a strong potential for short-term responses in surface and pore water, in the longer term as water table stabilises and vegetation starts to shift towards target communities (Hancock et al., in prep.; Bellamy et al., 2012) and natural-like nutrient cycling resumes (Nwaishii et al., 2016), it would be anticipated that water chemistry would also become similar to open bog (Haapalehto et al., 2014). Thus, water chemistry could potentially be used as a method to evaluate the effectiveness of restoration methods used as well as the recovery in forest-to-bog restoration sites over time. Part of this research explores this idea (Chapter 6).
1.5 Aim of this research

The scale of afforested blanket bogs in the UK coming to the end of their first rotation (Andersen et al., 2016), current government forestry policy (Forestry Commission Scotland, 2015) and peatland restoration targets (SNH, 2015) suggest that there will be increasing forest-to-bog restoration across Scotland and the British Isles. Given the importance of the Flow Country for soil carbon storage and provision of high water quality, it is essential to understand the impacts of this management practice here. The previous sections highlighted clear gaps which need to be addressed in terms of effects on the downstream aquatic ecosystem, effects of the carbon cycling through aquatic exports, and potential feedback with other peatland functions through disruption of nutrient cycling (Hancock et al., in. prep.; Rodgers et al., 2010; Andersen et al., 2013; Finnegan et al., 2014b; O’Driscoll et al., 2014a, 2014b; Ryder et al., 2014; Nwaishi et al., 2016). These issues are important in both the short time, in the immediate response to the disturbance of forest-to-bog restoration and in the longer-term recovery process (Figure 1.3). Therefore, the aim of this study is to determine the short (0-1 year) and long-term (1-17 years) impacts of forest-to-bog restoration on water quality and the export of aquatic carbon.

The specific objectives are:

1. To determine the effects of forest-to-bog restoration on pore and surface water quality in the first year post-restoration (Ch.3)

2. To assess the effects of forest-to-bog restoration on stream and river water quality in the first year post-restoration (Ch. 4)

3. To compare aquatic carbon export from an afforested catchment remaining as standing forestry, a blanket bog catchment and an afforested catchment, within which forest-to-bog restoration commenced, (0-1 year post-restoration; Ch. 5)

4. To evaluate the long-term (0-17 years) changes in pore and surface water quality across a chronosequence, as an indicator of restoration recovery following forest-to-bog restoration. (Ch. 6)
Figure 1.3: Current knowledge on hydrology and hydrochemistry of drained, afforested blanket bogs and those undergoing forest-to-bog restoration.
1.6 Thesis structure

The thesis structure follows these objectives. **Chapter 2** first introduces the field site: the RSPB Forsinard Flows National Nature Reserve and the background to forest-to-bog restoration on the reserve. It then describes the general sampling design for this research and the field and laboratory methods, which are common to more than one of the data chapters. **Chapter 3** investigates the short term effects of forest-to-bog restoration in pore and surface water quality, comparing two different restoration methods. **Chapter 4** assesses the combined effects of these restoration methods at a larger scale by investigating the effects on stream and river water quality and then interprets restoration effects in terms of mandatory water quality standards. **Chapter 5** focuses on aquatic carbon export in streams, assessing the short term impacts of forest-to-bog restoration. **Chapter 6** looks at the longer term recovery (0-17 years) in forest-to-bog restoration sites, through changes in pore and surface water chemistry at a chronosequence of sites undergoing restoration. In **Chapter 7**, a summary of the main findings from chapters 3-6 is presented and here we consider “the effects of bog restoration in formerly afforested peatlands on water quality and aquatic carbon fluxes” across spatial and temporal scales, along with the implications for management and peatland function.
2. Methods

2.1 Study site: Forsinard Flows National Nature Reserve

This study was conducted primarily on the Forsinard Flows National Nature Reserve (NNR; 58° 21’ 42.65” N, 3° 53’ 46.65” W) (Figure 2.1), managed by the nature conservation charity the Royal Society for the Protection of Birds (RSPB). The reserve is located in the north eastern side of the Flow Country (Caithness and Sutherland) with a temperate maritime climate, receiving an annual average precipitation of 970.5 mm and having a mean annual temperature of 11.4 °C (Kinbrace weather station 1981-2010: Hambley 2016). The reserve is managed for nature conservation and comprises of a high quality blanket bog habitat which attracts breeding populations of key wader species such as dunlin, green shanks and golden plovers (Stroud et al., 1987; Hancock et al., 2009).

Figure 2.1: Distribution of blanket bog (designated as Special Areas of Conservation (SAC)) across the Flow Country of Caithness and Sutherland (light blue shading with black borders shows SACs). Other black lines refer to additional SACs within the region. Blue hashed
areas with dark blue borders are the RSPB Forsinard Flows National Nature reserve (26 miles W-E). Pale green shaded areas are afforested (plantations) and the yellow star shows the Dyke Forest on the Forsinard Flows Reserve (the main site for this study).

The reserve covers a total area ~154 km², and comprises a mixture of open blanket bog, afforested bog with plantations of non-native conifers (planted mainly in the 1980s) and land undergoing forest-to-bog restoration. Forest-to-bog restoration has been carried out by the RSPB since 1997, as they acquired a number of non-native Sitka spruce (*Picea sitchensis*) and Lodgepole pine (*Pinus contorta*) plantations. Those afforested areas were felled to waste or harvested and forestry drains were blocked to raise the water table with an aim to restore the open blanket bog landscape. The ongoing restoration work has created a series of restoration areas, including a series of sites with different restoration ages (i.e., a chronosequence).

Over the 20 years since restoration on the reserve began, the continued growth of trees in plantations and advances in technology have influenced the restoration methods used (see Chapter 1.3.2). For example, in Talaheel (restored in 1997/98) the trees were less than 20 years old and small enough to be felled by chainsaw (Figure 2.2a). This doesn’t happen anymore: restoration is now being carried out with low ground pressure machinery to fell and harvest or mulch the 25+ year old trees.

### 2.2 Restoration in the Dyke forestry plantation

This study primarily focusses on the Dyke Forest restoration work, which began in 2014 (Chapters 3-5), with a smaller study on the chronosequence (Chapter 6). Forest-to-bog restoration in the Dyke Forestry plantation began in October 2014 (Figure 2.1) lasting until December 2015. Seven forestry blocks underwent restoration in that period (DK1-DK7; Figure 2.3). The centres of the blocks were chosen at random from 1km grid intersections within the Dyke forest, thus they were all at least 1km apart. Thus, these seven blocks were randomly selected to be representative of the wider Dyke Forest. In the planned design, each block was split into four contiguous monitoring plots of c.a. 4-6 ha (Figure 2.3), and each plot was allocated one of four restoration treatments. These
were intended to be combinations of standard or enhanced felling with collector drain and furrow blocking.

Figure 2.2: Restoration sites of different ages on Forsinard Flows NNR (a) Talaheel - restoration 1997/98 – small trees felled by hand into furrows. (b) Raphan – restoration 2011/12 – standard machine fell-to-waste plots – trees left in furrows, (c) Mulch plot in Raphan – restoration 2011/12, (d) Dyke – restoration 2014/15 – freshly mulched plot in foreground (~4 weeks prior to photograph), enhanced fell in background – awaiting harvesting. Credit for pictures: (a) M. Hancock, (b,c) J. Arne Subke, (d) P. Gaffney.

However, in practice only drain blocking was carried out (in main collector drains) within the timescale of this project, effectively giving two treatments; standard and enhanced felling. Additional areas outside the blocks also underwent restoration during this project, giving a total area of 174 ha. These areas were either necessary to restore to access the main blocks or were convenient to restore at this time because of their proximity to the main blocks. Restoration within the seven forestry blocks was carried out over a 10-month period (October 2014 to August 2015), with felling and harvesting complete on some sites before it started on others.
Figure 2.3: Seven restoration sites in Dyke Forest, chosen for forest-to-bog restoration by RSPB, beginning October 2014. Each block is named DK with a number and then split into four contiguous monitoring plots. Note that a matched forest control (to remain as forest) and a bog control (neither are shown on the map), are associated with each block. Restoration sites DK2, DK4, DK5 and DK6 were each sampled for this study; with DK 2,
DK4 and DK6 instrumented with piezometers for porewater sampling (Chapter 3). Black circles show stream and river sampling sites (Chapter 4), yellow squares show location of sites where aquatic carbon export was measured (Chapter 5), using automatic water samplers and flow gauging.

Therefore, not all the areas monitored in this study underwent restoration at the same time. For standard felling, the main stems were removed and the brash was laid in mats across the peat surface for the harvesting machinery to drive on. For enhanced felling, a similar approach was used but the brash mats were removed post-harvesting. Furthermore, standard and enhanced felling were carried out by different contractors using different machinery. Standard felling produced logs and brash mats using one machine which was a slower process overall but may have resulted in less disturbance to the peat surface. The stems were removed by a forwarder. Enhanced felling consisted of a felling-bunching machine (Figure 2.4a), brash stripper and sorting machine (Figure 2.4b) and a forwarder to remove the stems and brash. Stems were left on site for varying amounts of time depending on availability of machinery but on average for a period of three months, while brash was left on site for five months on some sites. As a final stage on enhanced plots, the removed brash was chipped at the roadside into HGVs and removed.

Where trees were too small to harvest economically, they were mulched to waste, without further treatment or removal of mulch material. There were fewer mulched sites (~10-15% total restoration area), than felled sites. Collector drain blocking was carried out by installing plastic pilling dams on the main collector drains in each plot (in both felling treatments), before the drain entered a watercourse (Figure 2.4 e-h). These were designed to prevent washing out of sediment to watercourses and help raise the water table. Dams were installed in triplicate within a section of collector drain between November 2013 and January 2014. Additionally, silt traps were added to collector drains at the time of felling. These were Hytex Terrastop® geotextiles installed across the drain upstream of plastic piling dams as an additional measure to reduce sediment transport to watercourses.
Figure 2.4: Restoration treatments in the Dyke Forest. (a) Feller-buncher machine used in the enhanced fell treatment (first stage) to fell trees and place into rows (panel d), (b) enhanced fell stage two - stripping brash from the stems, both of which are harvested in
2.3 Sampling in Dyke forestry plantation

The general sampling strategy, along with a summary of the measured water quality parameters are presented in this section. Methods which are common to multiple data chapters are described in this general methods chapter, those which are not are described in their respective data chapters.

2.3.1 Sampling design in Dyke forestry plantation

Four of the seven Dyke Forest restoration blocks to undergo forest-to-bog restoration in autumn 2014 were sampled in this study for stream water quality (DK2, DK4, DK5 and DK6; Figure 2.3). As the effects of restoration were investigated at both the pore- and surface-water, stream and river scales, the same blocks were used for pore and surface water sampling. However, due to time and resource constraints, only three were instrumented (with piezometers) for pore and surface water (DK2, DK4, DK6). These blocks were selected, mainly for practical reasons, after site visits to Dyke Forest. DK2 was selected as it was adjacent to the River Dyke and was the site of most concern with regard to effects on river water quality. The other two blocks (DK4, DK6) were chosen because they were accessible enough to make frequent sampling possible and along with DK2 gave good spatial coverage of the Dyke Forest. They are situated on either side of the River Dyke and contained a range in peat depths, slope and vegetation cover which is described in detail in Chapter 3.2.1 (Table 3.1).

Three forestry plantation and three open blanket bog control plots were also monitored and chosen from a selection of seven bog and seven afforested control plots. The afforested controls monitored in this study were matched by slope and size to plots within the restoration blocks (selected by RSPB). The open bog controls were selected for
practical reasons (i.e., ease of access and all on RSPB grounds) but were similar in peat depth and slope to the restoration plots (Chapter 3.2.1).

2.4 Field and laboratory measurements summary
Field sampling of pore, surface, stream and river water was carried out in order to assess a range of chemical and hydrological parameters, measured in the field or laboratory (Figure 2.5). Physico-chemical parameters of pH, temperature and conductivity were measured in the field using a Hanna HI 991300 multiparameter probe. Dissolved oxygen was measured using a YSI 556 MPS or a Hanna HI9828 probe. All probes were calibrated before use.

2.5 Laboratory measurements
All plastic and glassware used was first washed in 2% (v/v) Decon90® followed by thorough rinsing using Milli-Q water (18.2 MΩ resistivity). Plastic and glassware used for water sampling and analysis for metals and nutrients was additionally washed in 3.5 % (v/v) hydrochloric acid, followed by thorough rinsing using Milli-Q water.

![Diagram](image)

Figure 2.5: Summary of field and laboratory measurements conducted on pore, surface, stream and river water samples. Measurements performed only on stream and river water are underlined (Chapter 4). Measurements used in calculation of carbon exports are in bold (Chapter 5). WTD – water table depth, DOC – dissolved organic carbon, DIC – dissolved
inorganic carbon, TON - total oxidised nitrogen, SPM - suspended particulate matter, POC – particulate organic carbon, ANC – acid neutralising capacity.

2.5.1 Filtration and sample preparation for dissolved organic carbon (DOC), nutrients and element analysis

Chemical analyses for DOC, nutrients and metals were performed to quantify the dissolved fraction present in water samples. Standard practice in chemical analysis involves the separation of the solution (which contains dissolved components) and the solid phase (Rainwater and Thatcher, 1960; Hem, 1985). Generally speaking, it is the dissolved constituents that are available to biota and thus are most biologically relevant. Samples were therefore filtered to remove particulates before certain chemical analyses. Water samples were vacuum-filtered through 0.7 µm glass fibre filters (Fisherbrand MF300) which were pre-combusted at 450°C for six hours (Tappin et al., 2010). Glass fibre filters were chosen as they do not leach DOC into the samples and 0.7 µm was the smallest affordable pore size, commonly used in the literature for the measurement of DOC and POC (Strack et al., 2008; Waddington, 2008; Dinsmore et al., 2010). Filtrates were collected in 40 mL glass vials for DOC analysis, while a separate portion of filtrate was vacuum-filtered through 0.45 µm cellulose acetate filters (Sartorius Stedim) and collected into 50 mL polypropylene centrifuge tubes. Polycarbonate filter units (Sartorius) were used to allow direct collection into the desired containers (minimising sample contamination). A portion of sample (~5mL) was always used to pre-wash filters and was then discarded. Filtration was usually carried out within 24 hours of sample collection, and always within 48 hours. Samples were stored at 5ºC in the dark, prior to filtration. Procedural blanks (Milli-Q water) were also vacuum filtered using the same procedure, and in three of the pore water sampling rounds, field blanks were also used (Chapter 3.2). Samples for elemental analysis (macro and trace elements) were acidified with trace metal grade nitric acid at the ratio of 1 mL of acid per 20 mL of sample, in order to fix and preserve elements in solution and prevent any precipitation and/or binding to the storage tube surface (Clesceri et al., 1998). DOC and nutrient analysis was carried out on fresh samples, with analysis usually undertaken within two days of collection. Samples for elemental analysis were stored at 5ºC in the dark until analysis in large batches could be undertaken.
2.5.2 Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) analysis

DOC was determined using the high temperature catalytic combustion method (Sugimura and Suzuki, 1988) and a Shimadzu TOC-L instrument. The principle of analysis was to measure total carbon (TC) and then inorganic carbon (IC) which was then subtracted to calculate total organic carbon (TOC), termed DOC here as the samples were filtered. Internal standards of 20 mg L\(^{-1}\) TC and 10 mg L\(^{-1}\) IC were also prepared from refrigerated stock solutions (TC from potassium hydrogen phthalate, IC from sodium hydrogen carbonate and sodium carbonate; Nacalai Tesque Inc., Kyoto) and used as quality control standards which were tested before/after every 10 unknown samples. A lake water CRM (BIGMOOSE-02, Lot# 0412 Environment Canada) was also analysed periodically. The Shimadzu TOC-L generated a linear calibration for both TC and IC. Calibration curves (0-100 mg L\(^{-1}\) for TC and IC) were created periodically, on average, every 2-3 months as the instrument stability is very high. Re-calibration occurred when the carrier gas was changed or new standard stock solutions were made (1000 mg L\(^{-1}\) TC and IC). The most recent calibration curve in the system was used to determine DOC concentrations in the samples. Samples >100 mg L\(^{-1}\), were automatically diluted by the instrument, using an appropriate dilution factor. The instrument was programmed to measure all samples twice and perform a third measurement if the coefficient of variation of the first two peak areas was >2 % and then calculate a mean of all readings.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Certified values mg L(^{-1})</th>
<th>Measured average ± SD mg L(^{-1})</th>
<th>% Recovery*</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC</td>
<td>3.89 ± 0.37</td>
<td>3.98 ± 0.07</td>
<td>103.5% (n=6)</td>
</tr>
<tr>
<td>DIC</td>
<td>0.49 ± 0.27</td>
<td>0.49 ± 0.03</td>
<td>100.6% (n=6)</td>
</tr>
</tbody>
</table>

Table 2.1: Recoveries of certified reference material BIGMOOSE-02 (Lot# 0412, Environment Canada) for DOC and DIC analyses, using the Shimadzu TOC-L.

*Percentage recovery calculated also includes results of analysis of MAURI-09 (Lot# 913 and Lot# 815, Environment Canada) CRMs.
2.5.3 Nutrient analysis

Nutrient analysis was undertaken using a Seal AQ2 discrete analyser, to measure dissolved ammonium (NH$_4^+$), soluble reactive phosphate (SRP) and total oxidised nitrogen (TON), using adapted and validated methods as per ISO International water quality standards (http://www.seal-analytical.com/). The principles for these analytical techniques are well documented/understood and they represent standard methods used across research and the water analysis industry (ammonium; Harwood and Kuhn 1970, phosphate; Neal et al., 2000, TON; Moorcroft et al., 2001). Samples are mixed with aliquots of reagents by the auto-analyser, reactions occur in discrete reaction cells forming a coloured solution which is then measured spectrophotometrically. The intensity of the colour formed is proportional to the concentration of the nutrient. Certified reference materials (CRM) were also analysed to validate the analytical procedures (Fluka IC standards for phosphate and ammonium-nitrogen (1000 mg L$^{-1}$ diluted for use to 0.1 mg L$^{-1}$) and MERCK nitrate standard solution CRM (200 mg L$^{-1}$ diluted for use to 0.1 mg L$^{-1}$)). Calibration curves were plotted by the instrument using measurements taken from a range of standards prepared from ammonium chloride, sodium nitrate and potassium dihydrogen orthophosphate (Sigma Aldrich). These standards were run prior to and periodically during analysis to check for instrument drift. Samples at concentrations of >110% of the top standard were re-run using a (specified) auto-dilution.

The absorbance due to background colour in the samples (i.e., caused by DOC) was also measured using the AQ2 at each wavelength by replacing all reagents with Milli-Q water. This reading was then subtracted from the results to perform a colour correction (commonly required for peaty catchments; Murray 2012). If this is not undertaken, the background colour of the sample can elevate the absorbance reading.

Nutrient concentration data were manually calculated (in Microsoft excel) using raw calibration data from the instrument run. Similarly, limits of detection (LOD) were calculated using the standard deviation of blanks (Milli-Q water) analysed throughout the run:

\[
LOD = \text{average blank reading} + (3 \times \text{standard deviation of all blanks})
\]

\[\text{[Equation 2.1]}\]
where [average blank reading] is the average concentration in the Milli-Q water blanks in a run. The LOD was calculated individually for each instrument run and then an average LOD was calculated for all data (Table 2.4). Samples <LOD were then replaced with a value equal to 0.5*LOD as is common practice in analytical chemistry (Gotway et al., 1994; Clarke, 1998; Croghan and Egeghy, 2003).

Table 2.2: Recoveries of certified reference materials, limits of detection for nutrient analyses and mean procedural blank concentrations using SEAL AQ2, discrete analyser.

<table>
<thead>
<tr>
<th>CRMs</th>
<th>Certified values mg L(^{-1})</th>
<th>Diluted to: µg L(^{-1})</th>
<th>Measured average µg L(^{-1}) ± SD</th>
<th>Instrument LOD µg L(^{-1})</th>
<th>Mean procedural blank µg L(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH(_4^+)</td>
<td>Fluka 1000 ± 4</td>
<td>100</td>
<td>100.2 ± 18.3 (n = 89)</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>phosphate</td>
<td>Fluka 1000 ± 4</td>
<td>100</td>
<td>93.2 ± 11.8 (n = 82)</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>TON</td>
<td>Merck 198 ± 5</td>
<td>100</td>
<td>92.8 ± 12.9 (n = 85)</td>
<td>4</td>
<td>1</td>
</tr>
</tbody>
</table>

2.5.4 Analysis of macro and trace elements

Macro and trace element concentrations were determined by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) using a Varian 720 ES instrument (Clesceri et al., 1998). This instrument uses high temperature argon plasma to excite element atoms and measure concentration due to the intensity of a characteristic wavelength of light emitted as atoms fall from excited back to ground states. It also facilitates the simultaneous measurement of many elements (up to 78 at one time). Samples were analysed for concentrations of (i) base cations (Ca, Mg, Na, K), (ii) redox sensitive elements (Fe, Mn, Al, S) which in some cases are toxic to salmon and aquatic life (i.e., Al), and (iii) Cu, Zn and Ni, which are potentially toxic elements (PTE) above specific concentrations. Samples were diluted by a factor of two with Milli-Q water to reduce concentrations to within the linear range of the instrument. Standards were made using a mixture of single element ICP standards (Fluka), made into a multi-element intermediate standard which was then diluted further into five working calibration standards. Samples
with concentrations >110% of the top standard were re-run with a higher dilution factor (x6) until they fell within the calibration range. A river water CRM (MAURI-09 Lot# 913, Environment Canada) was also analysed during every instrument run for quality control purposes. The instrument was programmed to take five readings from each sample over 15 seconds whilst the sample was aspirated into the system - an average light emission intensity was thus generated and used to back-calculate to concentration in the sample. Concentration data and LODs were calculated as with nutrient analysis (Chapter 2.5.3).

Table 2.3: Recoveries of MAURI-09 (Lot #913, Environment Canada) certified reference material (analysed 106 times), instrument limits of detection (LOD) and mean procedural blank concentrations for macro and trace element analyses; the CRM only has certified values for selected elements, but measured values are presented for all elements. Next to the name of each element is the emission line wavelength used for measurement on the ICP-OES (Varian 720 ES).

<table>
<thead>
<tr>
<th>Element and emission wavelength</th>
<th>Certified values µg L⁻¹</th>
<th>Measured CRM values (average ± SD) µg L⁻¹</th>
<th>Mean % recovery</th>
<th>Instrument LOD µg L⁻¹</th>
<th>Mean procedural blank concentrations µg L⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium 396.152</td>
<td>76.6 ± 11.2</td>
<td>74.9 ± 12.0</td>
<td>98.2</td>
<td>1.5</td>
<td>6.3</td>
</tr>
<tr>
<td>Calcium 422.673</td>
<td>2950.0 ± 291.0</td>
<td>2846.9 ± 281.6</td>
<td>95.5</td>
<td>1.9</td>
<td>83.2</td>
</tr>
<tr>
<td>Magnesium 279.553</td>
<td>750.0 ± 61.6</td>
<td>780.9 ± 18.3</td>
<td>104.2</td>
<td>1.5</td>
<td>7.4</td>
</tr>
<tr>
<td>Potassium 766.491</td>
<td>406.0 ± 34.3</td>
<td>334.2 ± 28.9</td>
<td>81.4</td>
<td>2.8</td>
<td>46.3</td>
</tr>
<tr>
<td>Sodium 589.592</td>
<td>2190.0 ± 153.0</td>
<td>1889.5 ± 149.4</td>
<td>85.4</td>
<td>5.1</td>
<td>224.6</td>
</tr>
<tr>
<td>Sulphur 181.972</td>
<td>3780.0 ± 226.0</td>
<td>3849.2 ± 187.1</td>
<td>102.3</td>
<td>68.6</td>
<td>14.2</td>
</tr>
<tr>
<td>Copper 327.395</td>
<td>N/A</td>
<td>1.1 ± 1.8</td>
<td>N/A</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>Iron 238.204</td>
<td>N/A</td>
<td>103.2 ± 8.3</td>
<td>N/A</td>
<td>1.5</td>
<td>0.8</td>
</tr>
<tr>
<td>Manganese 257.610</td>
<td>N/A</td>
<td>0.5 ± 0.3</td>
<td>N/A</td>
<td>0.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Nickel 231.604</td>
<td>N/A</td>
<td>0.7 ± 4.6</td>
<td>N/A</td>
<td>4.4</td>
<td>2.5</td>
</tr>
<tr>
<td>Zinc 213.857</td>
<td>N/A</td>
<td>32.9 ± 72.7</td>
<td>N/A</td>
<td>1.2</td>
<td>11.1</td>
</tr>
</tbody>
</table>
2.5.5 Absorbance to measure organic matter quality
Absorbance of light by all samples was measured at 254 nm, 400 nm, 465 nm and 665 nm using a Camspec M350 UV/Visible spectrophotometer on 0.7 µm filtered samples (i.e., matched with the DOC analysis). Absorbance at 254 nm and 400 nm was used in conjunction with DOC concentration to give specific UV absorbance (SUVA), a useful indication of the proportion of coloured humic high molecular weight (HMW) substances in the DOC pool, commonly referred to as the colour to carbon ratio (Wallage et al., 2006; Wilson et al., 2011a). Absorbance at 465nm and 665nm (Abs465 nm/Abs665 nm) were also used as an approximation of the E4/E6 ratio (Chen et al., 1977), which is the ratio of humic to fulvic acids in the sample. Measurements were made in a quartz cuvette (transparent to UV light at 254nm (as opposed to glass or plastic)) with a path length of 1cm, and converted to the standard units of absorbance units per meter (Wallage et al., 2006; Wallage and Holden, 2010). The spectrophotometer was set to read zero at all wavelengths with Milli-Q water.

2.6 Statistical analyses
All the statistical analyses were performed using RStudio (Version 0.98.501, R Core Team 2016). The main methods used were Principal Response Curves (PRC; package vegan, Oksanen et al. 2016) and generalised linear mixed models (GLMMs; package lme4, Bates et al., 2015; package nlme, Pinheiro et al., 2016; package glmmPQL, Venebles and Ripley 2002) for water chemistry concentration data. The detailed procedures for each dataset are given in the appropriate chapters; here only a brief description of the methods is given. PRC is a multivariate method which compares the overall change in a dataset, over time to a chosen reference (van den Brink and Ter Braak, 1998, 1999). We used this to determine (statistically) how water chemistry from restoration sites differed relative to that of open bog and standing forest controls. The method produces a graphical output enabling visualisation of water changes chemistry following forest-to-bog restoration. PRC showed the strongest trends in water chemistry between treatments and controls but did not allow testing of the effect of restoration using on individual water chemistry variables. To do this GLMMs were used to test the effect of restoration relative to controls, accounting for both temporal and spatial autocorrelation (Crawley, 2007; Zuur et al., 2011).
3. Pore- and surface-water quality in the first year following forest-to-bog restoration

3.1 Introduction

In blanket bogs, hydrology and water chemistry interact together and with above and below-ground organisms and biogeochemical processes (Vitt and Chee, 1990; Belyea, 1996; Malmer, 2014). Water table depth (WTD) is a major control on peat formation, as when it is near the surface, saturated conditions slow down the decomposition of plant litter, allowing peat to form (Clymo, 1984; Chapter 1.1). Pore water (i.e. water within the peat matrix) chemistry influences decomposition by controlling availability of essential cations to micro-organisms (Thomas and Pearce, 2004; Gogo et al., 2010) and by influencing microbial community structure (Updegraff et al., 1995; Bridgham et al., 1996; Andersen et al., 2013a). Pore water chemistry is closely coupled with the chemistry of the peat matrix, through soluble decomposition products and cation exchange between the peat matrix and pore water (Wieder et al., 1985; Soudzilovskaia et al., 2010).

Furthermore, peat, pore- and surface-water chemistry are tightly coupled with blanket bog vegetation; gradients in chemical species influence both vascular plant and bryophyte distribution in bog and fen systems (Wieder et al., 1985; Chee and Vitt, 1989; Vitt and Chee, 1990). In blanket bogs, pore water is acidic and low in nutrients and metals (Glaser et al., 1981). This is associated with a unique vegetation mix of *Sphagnum* mosses, cotton grass (*Eriophorum* spp.), shrubs (*Myrica gale*) and carnivorous plants (*Drosera* spp.; Forrest and Smith, 1975), which are adapted to the low nutrient conditions and have developed different ways to obtain nutrients (Malmer et al., 2003). In turn, *Sphagnum* contributes to acidify its own environment further (Bell, 1959; Verhoeven and Liefveld, 1997; Rydin et al., 2006).

Pore and surface water chemistry are also influenced by environmental factors. For instance, increased evaporation during warmer weather can also lead to higher concentrations of solutes (Proctor, 2006; Andersen et al., 2010). Elevated temperatures are also associated with increasing decomposition rates within a soil and the associated production of soluble compounds (Updegraff et al., 1995). Prolonged oxidative conditions associated with drought can also increase pore water DOC production (Grand-Clement et al., 2014). However, during short-term droughts, significant reductions in pore
water DOC have been measured (Clark et al., 2012), along with increased acidity and sulphate concentrations, thus showing a complex temperature-moisture influence over pore water chemistry (Clark et al., 2009).

Land management can also have major influences on pore and surface water quality especially when vegetation, hydrology and/or nutrient cycles are modified. For example, peatland drainage can alter pore water chemistry by increasing the depth of the oxygenated layers (Holden et al., 2004) and the re-wetting of (formerly drained) open bog can result in very dynamic changes in pore water DOC (Fenner et al., 2011). Re-wetting of oxidised peat soils alters biogeochemical processes and can lead to significant increases in DOC in drainage waters within months (Chow et al., 2006), along with metals associated with DOC (Fenner et al., 2001). This is thought to be related to stimulated enzyme activity (Fenner et al., 2011).

In the context of forest-to-bog restoration, where the ultimate aim is restoration to an open bog habitat, the focus is on rewetting the peat, through drain blocking combined with tree removal (Hancock et al., 2014). So far, tree felling has also been found to increase nitrate, ammonium and phosphate concentrations in pore water under areas where brash has been left (Finnegan et al., 2012; Asam et al., 2014b). Excess nutrients are thought to result from both the cessation of uptake by trees and from brash and needle decomposition by microbes (Rosén et al., 1996; Hyvonen et al., 2000). These conditions feedback on microbial and vegetation communities (Bragazza et al., 2012b; Larmola et al., 2013) and will likely impact on the recovery process in forest-to-bog restoration sites. Although given sufficient time, belowground microbial and chemical functioning may return to conditions similar to open bog (Andersen et al., 2013b).

There is evidence of significant short-term changes from both drain blocking and felling when practised separately (Fenner et al., 2011; Asam et al., 2014b). However, the combined effect of drain blocking and conifer felling on pore and surface water is largely unknown. With 150 000 ha of deep peat (>50cm) afforested in Scotland and more in the rest of the UK (Morison, 2013; Forestry Commission Scotland, 2015), there is the potential for significant restoration in coming decades. Thus there is an important gap in knowledge. Significant changes in pore water chemistry may translate into deleterious impact in streams, lochs and rivers (Drinan et al., 2013). Successful establishment of target vegetation will also be closely linked to the below-ground chemical functioning
Therefore, it is important to understand the short-term effects of this land-use change on pore and surface water both from a water quality and a below-ground biogeochemistry perspective.

3.1.1 Chapter aims
This chapter addresses this gap, through three specific objectives: 1) To determine the short-term effects (up to 1 year) of forest-to-bog restoration on pore and surface water chemistry; 2) to evaluate how seasonality and management interact with pore water chemistry and hydrology; 3) to measure the contributions of peat, needles and brash to pore water chemistry in a controlled laboratory leaching experiment. It was hypothesised that: 1) in the short term, forest-to-bog restoration would increase pore and surface water concentrations of DOC, nutrients and metals; 2) restoration management would enhance the natural seasonal fluctuations observed in water chemistry relative to open bog and afforested controls; 3) the addition of brash and needles would significantly increase DOC, nutrients and metal concentrations in pore water.

3.2 Methods
3.2.1 Site description
Forest-to-bog restoration in the Dyke Forest, RSPB Forsinard Flows National Nature Reserve commenced in October 2014 over seven replicated restoration blocks (Chapter 2.2; Figure 2.3). Three of these were selected for monitoring of pore and surface water; DK2, DK4, DK6 (Figure 3.1). These blocks, were spread across the Dyke Forest on either side of the River Dyke and represented a range of physical conditions across the forest (Table 3.1). These blocks were also used in stream water monitoring (Chapter 4) thus allowing the water quality effects of forest-to-bog to be considered at multiple scales (Chapter 7).

At the beginning of this study (May 2013), each of these blocks were still under standing forestry with a mixture of non-native Sitka spruce (*Picea sitchensis*) and Lodgepole pine (*Pinus contorta*), planted between 1982 and 1989. Restoration in DK2 and DK4 began with tree felling in October 2014, while in DK6 felling commenced in March 2015. All
felling and harvesting work on these blocks was complete by August 2015. Each block contained two plots restored by standard felling (stem harvest, brash left on site) and two restored by enhanced felling (stem plus brash harvest: Chapter 2.2). In DK2 and DK4, small areas (18% and 38%, respectively) were also mulched in standard fell plots, where trees were uneconomical to harvest. The main forestry drains in each plot were blocked (plastic piling dams in triplicate) prior to the drain entering a water course. Additionally, Hytex® geotextile silt traps were installed upstream of drain blocks. The sampling design also included three standing forest control plots and three open bog control plots, which were instrumented identically to restoration plots. Sphagnum spp. only dominated in open bog control plots, while other mosses and vascular plants were the dominant groups in afforested and restoration plots (Table 3.1)

3.2.2 Pore water sampling

Pore water sampling was carried out using piezometers which were inserted into the peat for depth specific sampling. Piezometers were constructed from 32 mm (internal diameter) polypropylene piping (Toolstation, Waste Piping) soaked overnight in 2% decon90® for cleaning to laboratory standards before installation. A 10 cm screen of holes was drilled in each piezometer consisting of lines of 3 mm holes spaced 1 cm apart in alternately matched lines (Figure 3.2). Polypropylene milk bottle tops were used as lids and attached to the base of piezometers (cleaned in 2% decon90® and held in place with Gaffatape®). A layer of Apollo frost fleece® was wrapped around the screen to prevent peat clogging the piezometer holes. As a material not normally used Apollo frost fleece® was also tested for its ability to leach DOC into water samples in a series of experiments (Appendix 3.1). These experiments confirmed its suitability for use.
Figure 3.1: Forest-to-bog restoration and control plots for Dyke Forest, where pore and surface water were monitored: Orange plots are restoration areas (felling and harvesting between October 2014 – August 2015) – each restoration block (DK2, DK4, DK6) contained two plots of standard felling and two plots of enhanced felling (see section 3.2.1). Yellow
plots are standing forest controls (Y plots) and blue plots are open bog controls (Z plots). Precipitation was sampled from locations marked (▼).

Table 3.1: Restoration blocks and control plot characteristics – averages for all plots in each block. Vegetation data from RSPB Forest-to-Bog project (M. Hancock, personal communication, 2016; assessed by recording dominant vegetation on a monthly basis, at five points in each plot, which were initially randomly chosen).

<table>
<thead>
<tr>
<th>Block</th>
<th>Planted</th>
<th>Restoration</th>
<th>Vegetation – recorded at five selected points - Oct 2012-Sep 2013: % points with dominant substrate (vegetation type)</th>
<th>Mean plot area (ha)</th>
<th>Mean peat depth (cm)</th>
<th>Slope degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Mean</strong></td>
<td>VP</td>
<td>OM</td>
<td>SP</td>
</tr>
<tr>
<td>DK2</td>
<td>1983</td>
<td>Oct 14- Nov 14</td>
<td>Oct 14- Dec 14</td>
<td>May 15</td>
<td>42.7</td>
<td>52.3</td>
</tr>
<tr>
<td>DK4</td>
<td>1984, 1989</td>
<td>Oct 14-Feb 15</td>
<td>Mar 15-Apr 15</td>
<td>May 15</td>
<td>25</td>
<td>72.1</td>
</tr>
<tr>
<td>DK6</td>
<td>1982, 1988</td>
<td>Mar 15-Jun 15</td>
<td>May 15-Jul 15</td>
<td>Aug 15</td>
<td>51.9</td>
<td>39.7</td>
</tr>
<tr>
<td>BOG</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>11.6</td>
<td>37.4</td>
<td>38.4</td>
</tr>
<tr>
<td>FOR</td>
<td>1984, 1989</td>
<td>-</td>
<td>24.4</td>
<td>63.3</td>
<td>11.7</td>
<td>0</td>
</tr>
</tbody>
</table>

Key to substrate type:
- **VP**: Vascular plants & their litter (graminoids + ericaceous shrubs)
- **OM**: Other mosses (pleurocarpus mosses +acrocarpus mosses + others)
- **SP**: Sphagnum
- **LI**: Lichens
- **NL.B**: Needle litter & bare soil

Transects of four piezometer 'nests', each incorporating one shallow and one deep piezometer, were installed along the slope in each restoration and control plot (Table 3.2). Shallow and deep piezometers were installed to represent functional depths within the peat profile. Shallow piezometers designed to collect pore water from the zone within which water table is likely to fluctuate and deep piezometers were designed to collect water from the permanently waterlogged zone (Figure 3.2). Shallow piezometers were installed at sampling depths of -30 to -40 cm in afforested / restoration plots and -20 to -30 cm in open bog controls, while deep piezometers were at a maximum depth of -85 cm (less if the peat was shallower). Each transect also had at least one dipwell for manual WTD measures during pore water sampling (Figure 3.2).
One some occasions (particularly during dry summer months), there were no samples collected in shallow or deep piezometers, as water tables were lower. This suggests there were periods of aeration in the peat. This occurred more often in shallow piezometers, which were installed in the regions where water normally table fluctuates. Therefore, samples were missing on some occasions and the total number collected was less than the total number of piezometers indicated in Table 3.2

Table 3.2: Pore water sampling design

<table>
<thead>
<tr>
<th>Land Use</th>
<th>treatment</th>
<th>No. replicated blocks</th>
<th>No. plots of per block</th>
<th>No. plots of each treatment</th>
<th>Total no. shallow PZs</th>
<th>Total no. deep PZs</th>
<th>Total no. PZs</th>
</tr>
</thead>
<tbody>
<tr>
<td>RESTORATION</td>
<td>standard</td>
<td>3</td>
<td>2</td>
<td>6</td>
<td>24</td>
<td>24</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>enhanced</td>
<td>3</td>
<td>2</td>
<td>6</td>
<td>24</td>
<td>24</td>
<td>48</td>
</tr>
<tr>
<td>OPEN BOG</td>
<td>bog control</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>12</td>
<td>12</td>
<td>24</td>
</tr>
<tr>
<td>AFFORESTED</td>
<td>forest control</td>
<td>3</td>
<td>1</td>
<td>3</td>
<td>12</td>
<td>12</td>
<td>24</td>
</tr>
<tr>
<td>TOTALS</td>
<td></td>
<td>20</td>
<td>72</td>
<td>72</td>
<td></td>
<td></td>
<td>144</td>
</tr>
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In each plot, a transect of four piezometer (PZ) nests was installed, each nest including one ‘deep’ and one ‘shallow’ PZ (Figure 3).

Pore water sampling in the Dyke Forest and control sites commenced in May 2013 initially at six week intervals to gather data on pore water quality prior to forest-to-bog restoration, which was planned for autumn-winter 2013. From October 2013, sampling frequency was decreased to three months, as restoration was delayed until autumn-winter 2014. There were approximately six month gaps during the main restoration period in each block (Table 3.1) as access was not permitted when machinery was operating. Piezometers were emptied four-six days prior to sample collection, to allow fresh pore water to enter the sampler (Strack et al., 2008). The volume in each piezometer was recorded at emptying and sampling, as well as height of the top of the piezometer above the vegetation surface. Samples were collected into LDPE bottles (Nalgene) using a syringe connected to flexible PVC tubing pre-rinsed with 5 mL of sample. A subsample (~15 mL) was used for field measurement of physico-chemical parameters (temperature, pH and conductivity; Chapter 2.4).

3.2.3 Surface water sampling

Surface water was sampled from collector drains within each of the forest and restoration plots. These drains acted like small ‘catchment’ channels for surface and near surface flow – and later merged into the nearest stream or river (Figure 3.2). In open bog control sites, there were also drainage ditches present which had been blocked in 1996 and 2004 but allowed a comparable sampling strategy. There was at least one surface water sample
collected per plot, allowing a comparison of surface water across all treatments. Where piezometer transects passed through more than one collector drain, additional drains were sampled but samples analysed individually. In open bog and afforested control plots, surface runoff was also collected using crest tubes (small piezometers which only collect surface runoff water).

Figure 3.2: Schematic of pore and surface water sampling protocols. (a) piezometer design (a 10 cm screen of holes was drilled in each piezometer consisting of lines of 3 mm holes spaced 1 cm apart in alternately matched lines), with milk tops at the base and top, (b) piezometer nest (one deep, one shallow) in an afforested control plot, (c) pore water sampling from piezometers in an open bog control plot and (d) piezometer transect (in an afforested plot). One transect was installed in each monitoring plot, which comprised of four nests of piezometers. Transects included a dipwell next to one of the piezometer nests in a random position. The lines on each tube indicate the region drilled with holes. Each transect contained at least one collector drain, where surface water was collected. In each piezometer nest, the deep piezometer was installed in the permanently waterlogged zone and one shallow piezometer in the zone around which the water table fluctuates. In panel (d), the
water table is lower than shallow piezometers but moves periodically depending on hydrological conditions. In this sampling design in restoration plots, it was anticipated that following the start of restoration the water table would rise; therefore, shallow piezometers would collect samples from the newly re-wetted zone, where the most dynamic changes in pore water chemistry may be occurring.

There were two crest tubes per plot, at opposite ends of the piezometer transect. In open bog plots crest tubes were installed next to piezometers, while in afforested control plots crest tubes were installed in plough furrows to capture surface runoff. Surface water was sampled from October 2013 to December 2015. pH, conductivity and temperature were also measured in the field.

3.2.4 Precipitation sampling
In 2015 precipitation samples were also collected from two locations for chemical analysis (Figure 3.1) which were approximately 7km apart and at either side of the study area. Precipitation collectors were constructed from 500 mL HDPE bottles with funnels attached to the mouths. Precipitation was sub-sampled with a syringe connected to flexible PVC tubing into a 125 mL HDPE bottle, with pH, conductivity and temperature measures made in the field.

3.2.5 Preparation and analysis of samples
Samples were refrigerated at 4°C on return to the laboratory and filtered normally within 24 hours of collection (always within 36 hours) as described in Chapter 2.5. They were then analysed for concentrations of DOC, NH₄⁺, NO₃⁻, soluble reactive phosphate (SRP) and a suite of macro (Ca, K, Mg, Na, S) and trace elements (Al, Cu, Fe, Mn, Ni, Zn) following the protocols described in Chapter 2.5. DOC quality was also measured by absorbance (Chapter 2.5).

3.2.6 Experiments of DOC, nutrient and metal leaching from peat, needles and brash
Laboratory experiments were performed to test the effect of peat, needles and brash on water chemistry in a controlled environment. Peat cores were collected from afforested
sites, along with fresh brash taken from Sitka spruce and Lodgepole Pine trees. These were placed into plastic columns (n=5) either as peat only (P), peat + needles (P+N), peat + needles + brash (P+N+B). Precipitation (200-400 mL) was added and percolated through the column and was left for 24 hours or nine days, as a maximum period between bailing and emptying piezometers. Water samples were collected from the peat, needle and brash layers respectively. Further methods are described in Appendix 3.2.

3.2.7 Statistical analyses
All the statistical analyses were performed using RStudio (Version 0.98.501, R Core Team, 2016). All plots in restoration blocks (DK2, DK4, DK6) were compared with afforested and open bog controls, in a before-after-control-impact (BACI) design (Stewart-oaten et al., 1986). Each plot was assigned to a class of open bog (BOG), afforested (FOR), restoration standard felling (STD) or restoration enhanced felling (ENH). As there were two restoration treatments (standard and enhanced felling) in each block (of four plots), this gave two replicates of each treatment per block and six replicates overall. There were three replicates of afforested and open bog control plots. Each plot contained four piezometer pairs, which were considered repeated measures within the plot, therefore replication was at the plot level. For surface water samples, results from drain and crest tube samples were combined.

To look at the overall changes in water chemistry of the plot classes over time, we used principal response curves (PRC; package vegan, Oksanen et al., 2016), which allowed all classes to be compared to a chosen reference, which was the BOG control plots (van den Brink and Ter Braak, 1998, 1999). This multivariate method specifically tested the time by treatment interaction for a response matrix (log10(x+1) transformed water chemistry variables), enabling the visualisation and testing of temporal trends in a given class in relation to the reference set a priori (Andersen et al., 2010). Temporal trends were visualised as deviations from the reference rather than absolute values, with each class represented by a response curve. In addition, as this method was based on a redundancy analysis (RDA), it displayed the strength of the different water chemistry variables with these temporal trends (van den Brink and Ter Braak, 1999). The significance of the principal response curves was tested using Monte Carlo permutations (n=999).
The PRC analysis was used to assess which water chemistry variables differed most from the bog reference over time. Variables which scored strongly (< -0.5 or > +0.5; van den Brink and Ter Braak, 1999) were tested using univariate statistics to look for significant effects of restoration on concentrations in the treatments relative to controls. The PRC suggested that most of the key water chemistry variables we hypothesised to be affected by restoration should be tested, except NH$_4^+$ and pH. As these are both key elements to bog functionality they were included in univariate analysis along with WTD.

Univariate statistical analysis was carried out at the class level using linear and generalised linear mixed models (LMMs and GLMMs) with the functions lme (package nlme, Pinheiro et al., 2016) and glmer (package lme4, Bates et al., 2015) to test the effects of time (pre- / post-restoration) and management. As a simpler (linear) model structure LMMs were first used. Where data could not be modelled using LMMs (poor model fit), they were modelled using GLMMs by varying the error family and link functions until the best model fit was found and lowest Akaike’s Information criterion (AICc) value (Thomas et al., 2013). Appropriateness of model fit was checked by normality of residuals and homoscedasticity of residuals (Crawley, 2007; Zuur et al., 2011). Data were modelled both as transformed (LOG$_{10}$(x+1)) and untransformed to look for best fit.

Class (BOG, FOR, STD and ENH), restoration period (pre- and post-restoration) and the interaction term class*restoration were fixed factors. To account for repeated measures over time, “sampling season number” was added as a random slope (compound symmetry) as each sampling round generally took more than one month to complete. “Plot” was added as a random intercept as sampling sites within each class, as there were several plot replicates in each class which were not assumed to have the same starting point in water chemistry. Wald chi-square tests (function Anova, package car, Fox and Weisberg, 2011) of the model fixed effects were carried out to determine if the interaction term was significant. Thus we used primarily the class*period interaction to test for a difference in treatments, relative to the BOG and FOR controls. If the interaction was significant we used a posteriori comparison using least squares means (function lsmeans, package lsmeans, Lenth, 2016), to test for significant differences between classes (treatments) in the pre- and post- restoration periods.

There were some variables (phosphate and NH$_4^+$) which had poor fit (heteroscedasticity of variance) when modelled using LMMs or GLMMs, generally because of a higher
percentage of data < LOD, where these data were replaced with 0.5*LOD. This problem was overcome by using generalised least squares models (GLS) using function *gls* (package *nlme*, Pinheiro et al., 2016). These heterogeneous variance models allowed the variance structure to be specified, by accounting for variation within each level of the factors “class” and “fell” and for the “season number” and “plot” as the two random terms in the model using the *varIdent, varFixed* and *varComb* functions (package *nlme*, Pinheiro et al., 2016). In adding in each of these variance structures the AIC values were compared (Thomas et al., 2013) and the lowest AIC was when all were included. Checks of model fit (normality of residuals and homoscedasticity) and for significant interactions followed by *a posteriori* comparison using *lsmeans* were carried out as above.

In the main statistical analysis, comparisons were between BOG, FOR, STD and ENH classes. Included in the STD class, were a small number of piezometer nests and surface water sampling sites within areas which were mulched (MUL; \( n=6 \) nests for pore water, \( n=2 \) sites for surface water). The main experimental design was to compare STD and ENH treatments with MUL plots included within them. As mulching was carried out on crop failure areas (small trees - not economical to harvest), these may have been atypical sites. Given this, with the small number of MUL plot measurements, we carried out a qualitative comparison of DOC, phosphate and K concentrations. For this we used STD and ENH plots from DK2 and DK4 (only blocks with mulching), sampled MUL sites and their corresponding BOG and FOR controls (2Z, 1Z, 2Y, 4Y; Figure 3.1).

Univariate statistical analyses of the peat, needle and brash leaching experiments were carried out using generalised linear models (GLMs; function *glm*, package *stats*, R Core Team, 2016; Appendix 3.2). In this case there was only one factor (class) to test for differences in water chemistry between precipitation, water extracted from brash (B) and needle (N) layers (P+N+B treatment only) and from the peat (P) layer (P, P+N, P+N+B treatments). Only the P+N+B treatment had water remaining in the needle layer at sampling time. GLM fit was checked in the same way as for GLMMs (described above) followed by *a posteriori* comparison (function *lsmeans*, package *lsmeans*, Lenth, 2016) to determine which treatments were significantly different (where appropriate).
3.3 Results

3.3.1 Overall patterns of spatio-temporal change in water chemistry

The temporal patterns in water chemistry differed significantly between the reference sites (bog control; BOG) and the afforested controls (FOR), enhanced felling sites (ENH) and standard felling sites (STD) for surface water \(F=141.2, p=0.001\); Figure 3.3a), shallow pore water \(F=74.0, p=0.001\); Figure 3.3b) and deep pore water \(F=45.7, p=0.001\); Figure 3.3c). For surface water, in the pre-restoration period, the ENH and STD plots were similar to FOR plots but different from the bog reference (Figure 3.3a). Following restoration from June 2015, there was a decoupling of the ENH and STD and FOR, as the former moved further away from the BOG reference. The concentrations of DOC, K and phosphate and the conductivity, which were lower in the bog reference than in all other classes, increased even further following restoration management in STD and ENH surface water samples. Towards the end of the monitoring period, these parameters were decreasing again in ENH but still appeared to be rising in STD plots.

In shallow pore water, the FOR and restoration plots consistently showed higher DOC, conductivity, Ca and Na than the BOG reference (Figure 3.3b). However post-restoration there appeared an increase in these parameters in ENH and STD plots from June 2015. By December 2015, the trend began to decrease back towards the BOG reference. In deep pore water, water chemistry changes were less pronounced. The greatest difference between the BOG reference sites and the ENH and STD classes was in June 2015 (post- restoration period), where DIC decreased in the latter, but DOC, S, conductivity and Mg increased (Figure 3.3c). The FOR plots exhibited a similar pattern but with a slight time lag. The deep pore water chemistry of ENH and STD plots was most similar to each other in the post-restoration period.
Figure 3.3: Principal response curves for water chemistry for (a) surface water, (b) shallow pore water and (c) deep pore water. The left side of each panel represents overall deviation from the reference open bog control sites (BOG), for the other plot classes (afforested control sites (FOR), enhanced restoration sites (ENH), and standard restoration sites (STD)). This is expressed as a canonical coefficient on the first principal component axis (PC1), in comparison with the reference open bog control sites – represented by the zero line. The right hand side of each panel shows canonical coefficients for all the elements interpreted. A more positive the coefficient shows a stronger relationship with the curve, while a more negative coefficient suggests the opposite trend to the curve. The water chemistry parameters most strongly associated with the curves are therefore those, with the highest and lowest coefficients (green shading). 0.5 was used as the threshold to denote the main water chemistry parameters driving the trend (green broken line and arrow), with parameters scoring >0.5 or <-0.5 analysed with univariate statistics (section 3.2.7). The grey panels show the period when forest-to-bog restoration management was occurring (October 2014 to August 2015). For shallow and deep pore water (b,c) the graph extends from June 2013 to December 2015, whereas for surface water (a) sampling was from February 2014 to December 2015, hence the grey panel is wider. Phosphate is abbreviated to Phos, conductivity to Cond, temperature to Temp.

3.3.2 Main effects of forest-to-bog restoration on water chemistry and hydrology
Following forest-to-bog restoration there were significant increases in DOC, NH₄⁺, phosphate and K in surface water and shallow porewater (Table 3.2). Ca and Na were found to have a significant (treatment*period) interaction term in both shallow and deep porewater, although only deep porewater Ca in STD plots appeared to increase significantly post-restoration. In deep porewater there were additionally significant increases in DOC, Mg and conductivity post-restoration. pH was found to change significantly in surface water, where there was a significant increase.

In 2014 there were larger precipitation events but there were also more drought periods in the summer than in 2015 (Figure 3.4b). Mean daily air temperature showed a similar annual cycle in both 2014 and 2015 with warmer summer temperatures in 2014 (Figure 3.4a). WTD increased post-restoration in both ENH and STD plots respectively (X=13.64, p=0.0034; Table 3.2). In 2013 (pre-restoration) WTD was at lowest levels in all plot classes (Figure 3.4c).
Table 3.3: Summary of significant changes in pore and surface water chemistry and WTD following forest-to-bog restoration using linear mixed models (function lme), generalised linear mixed models (function glmer), and generalised least squares (function gls). Wald chi-square tests of the model fixed effects were carried out to determine if the interaction term was significant. Thus we used primarily the treatment-period interaction to test for a difference in treatments, relative to that of FOR and BOG controls (i.e. an effect of restoration). If significant (marked in bold), these were followed by Tukey pairwise comparisons (function lsmeans), where letters (CLDs) were derived. Treatments with the same letters were not significantly different. Concentrations are means ± SE for each class in pre- and post-restoration periods respectively (n = no. samples). Phosphate has been abbreviated to Phos, conductivity to Cond, temperature to Temp.

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Figure 3.4: Time series of (a) mean daily air temperature and (b) daily precipitation from December 2013 to December 2015 recorded in an open bog site, (c) mean water table depth (WTD) ± SE from May 2013 to December 2015 for each plot class per sampling round. Grey shading represents period of forest-to-bog restoration (Oct 14 to Aug 15).
3.3.2.1 DOC and plant nutrients

Post-restoration, DOC concentrations increased significantly in both STD and ENH plots at the three depths measured (Figure 3.5a; p values Table 3.2). The increases in surface and shallow pore waters (≥ 2 fold) occurred from June 2015 where mean concentrations peaked at ~150 mg L⁻¹ in ENH plots and slightly lower in STD plots in September 2015 (Figure 3.5a). By December 2015 mean DOC concentrations decreased slightly. In deep pore water mean concentrations increased (35-40%) to ~75 mg L⁻¹ post-restoration and remained at this level (Figure 3.5a). In terms of DOC quality, the E4:E6 ratio decreased post-restoration in surface water and shallow pore water, in ENH and STD treatments but this was within the range BOG and FOR controls (data not shown).

NH₄⁺ concentrations increased in shallow pore water (X=59.90, p<0.0001) and surface water (X=32.33, p<0.0001) following restoration, relative to FOR and BOG controls (Figure 3.5b). In surface water this increase was only in ENH plots (8 fold increase), while in shallow pore water both ENH and STD increased (4 and 15 fold respectively). Post-restoration, the highest mean NH₄⁺ concentrations were in shallow pore water STD plots. NH₄⁺ concentrations were higher in deep pore water, compared to shallow and surface, in which FOR sites had more than double that of other classes at times (Figure 3.5b). However, there were no significant changes in deep porewater NH₄⁺ concentrations following restoration.
Figure 3.5: Time series of (a) dissolved organic carbon (DOC), (b) ammonium (NH₄⁺), (c) phosphate, (d) potassium (K) in surface water (top panels) from October 2013 to December 2015, shallow pore water (middle) and deep pore water (bottom) from May/June 2013 to December 2015. Plots are mean values ± SE for each plot class per sampling round. Grey shading represents period of forest-to-bog restoration (Oct 14 to Aug 15).
Following restoration, phosphate and K increased significantly in surface water (X=137.86, p<0.0001 and X=35.68 p<0.0001, respectively). Concentrations increased sharply in both ENH and STD treatments (between 8 and 99 fold) from June 2015 and for both variables, highest mean concentrations were in ENH plots (Figure 3.5c,d). In shallow porewater, phosphate concentrations increased significantly post-restoration (X=53.68 p<0.0001), by 6- and 33-fold in ENH and STD plots respectively (Figure 3.5c). In STD plots, post-restoration concentrations were similar to that of surface water, while the increase in ENH plots was smaller, although they appeared to continue increasing into December 2015. In deep porewater, concentrations increased almost 5-fold following restoration in ENH plots. K increases, were much less pronounced in pore water.
compared to surface water (Figure 3.5d). In shallow porewater concentrations increased significantly (X=21.21 p<0.0001) by 3-fold, with slightly higher concentrations in STD plots. There appeared to be no effects of restoration on deep pore water K.

### 3.3.2.2 pH, conductivity and metals

Generally, across the whole study, pore water and surface water pH was highest in open bog (BOG; Figure 3.6a; mean pH 4.1-4.6) and was found to increase significantly following restoration only in surface water (X=24.90, p<0.0001). However, in surface water, pH was significantly higher in BOG, ENH and STD classes post-restoration compared to their respective pre-restoration levels (Table 3.2). In shallow and deep pore water, (Figure 3.6a) pH followed a similar temporal trend in treatments and controls.

In surface water, Ca concentrations appeared to increase post-restoration (not tested), with highest concentrations in ENH plots, which increased (1.7 fold) compared to pre-restoration (Figure 3.6b). In shallow and deep pore water the only changes in restoration plots were a 40% increase in STD plots (deep pore water) with no other apparent effects of restoration. Ca concentrations were similar in shallow and deep pore water and were generally lowest in BOG sites.

In deep pore water there were small but significant increases in conductivity and Mg post restoration (X=10.13, p=0.0175, X=8.37, p=0.0389 respectively). Only STD plots showed an increase as concentrations were similar pre- and post-restoration in ENH plots (Figure 3.6c,d). Despite, scoring highly on the PRC analysis neither Mg or conductivity changed significantly following restoration in shallow pore water or surface water. This was also the case for Na, which showed no apparent effects of restoration.

Al, Mn and Fe in surface water were low scoring elements on the PRC, yet each showed slight concentration increases in surface water post restoration, which were greatest in ENH plots (Figure 3.7a,b,c). A similar trend was observed for Fe in shallow porewater in both felling treatments. While Fe and Mn peaked in summer/ autumn, Al concentrations continued to increase into December 2015. In general, our results showed greatest concentration increases in surface water, although DOC and plant nutrients also exhibited strong increases in shallow porewater, while deep porewater showed smaller changes.
Figure 3.6: Time series of (a) pH, (b) calcium (Ca) in surface water (top panels) from October 2013 to December 2015, shallow pore water (middle) and deep pore water (bottom) from May 2013 to December 2015, (c) conductivity and (d) magnesium (Mg) in deep pore water from May 2013 to December 2015. Plots are mean values for each class ± SE. Grey shading represents period of forest-to-bog restoration (Oct 14 to Aug 15).
Figure 3.7: Time series of (a) aluminium (Al), (b) iron (Fe), (c) manganese (Mn) in surface water from October 2013 to December 2015, (d) iron (Fe) in shallow pore water from May 2013 to December 2015. Plots are mean values for each class ± SE. Grey shading represents period of forest-to-bog restoration (Oct 14 - Aug 15). These parameters were not tested using univariate statistics, as were ‘low’ scoring on the PRC.

3.3.3 Assessment of mulching on pore and surface water DOC, phosphate and potassium concentrations

Mulched (MUL) sites had slightly higher surface water mean DOC concentrations than in adjacent ENH or STD treatments (Figure 3.8a). Additionally, in shallow pore water in MUL sites, concentrations continued to increase into December 2015, where DOC reached higher levels than the peaks in adjacent ENH and STD fell treatments. MUL sites showed greater increases in phosphate concentrations compared to the adjacent felled plots in surface water and particularly in shallow pore water (Figure 3.8b; highest field phosphate measured in study). This was also observed for K concentrations in shallow pore water although in surface water mean K in MUL sites was similar to ENH and STD plots (Figure 3.8c). However, as MUL sites represent failed crop areas (small trees) they may be less comparable with STD and ENH sites.
Figure 3.8: Time series of (a) dissolved organic carbon (DOC), (b) phosphate, (c) potassium (K) in surface water (top) from October 2013–December 2015, shallow pore water (middle) and deep pore water (bottom) from May/June 2013 to December 2015. Plots are mean values ± SE for each plot class per sampling round, comparing STD and ENH treatments with mulching (MUL; in blue) and FOR and BOG controls. These plots include only data from DK2 and DK4 and their respective FOR and BOG control plots, as no mulching was carried out in DK6. Grey shading represents period of forest-to-bog restoration (Oct 14 - Aug 15). As MUL sites were areas of crop failure (small trees) they may be atypical, therefore no statistical comparison was carried out.
3.3.4 Peat, needle and brash leaching experiments

The peat + needle + brash (P+N+B) treatment led to the largest increase in DOC in leaching water in the nine-day exposure, which was the only significant treatment effect on DOC (Figure 3.9a). Highest DOC concentrations were found in the needle and brash layers (mean ~ 540 mg L\(^{-1}\)), although the peat + needle (P+N) and peat (P) treatments, both leached DOC, producing some concentrations of several hundred mg L\(^{-1}\) (higher than field pore water measures). In the 24 hour experiment the P+N+B and P+N treatments leached most DOC with mean concentrations ~120 mg L\(^{-1}\) (Figure 3.9a).

For K, highest concentrations were found in the brash and needle layers of the P+N+B treatment in the nine-day experiment (Figure 3.9b), with mean concentrations in the brash layer > 50 mg L\(^{-1}\) (peak mean in field ~8 mg L\(^{-1}\) K in surface water). P+N+B also leached most K in the 24 hour experiment and in both experiments the P and P+N treatments both leached lesser quantities of K. The highest phosphate concentrations were in the P+N and P+N+B (peat layer and needle layer) treatments in the nine day experiments (Figure 3.9c). In the 24-hour experiment, mean phosphate concentrations were much lower (>factor of 50) but the highest concentrations were again in the needle layer of P+N+B treatment.

The highest NH\(_4^+\) concentrations were found in the peat and needle layers of the P+N+B treatment in the nine-day experiment. The mean concentration of NH\(_4^+\) in precipitation was however high to begin with (~2 mg N L\(^{-1}\); Figure 3.9d). In the 24 hour experiment the precipitation and maximum leached concentrations of NH\(_4^+\) were much lower (>factor of 70), but maximum concentrations were found in the needle layer. In both the nine day and 24 hour experiments, the mean Mn concentrations were lower than the other variables across all treatments. However, the P+N+B treatment contributed most Mn in the needle and peat layers (Figure 3.9e). For Al, maximum concentrations were found in the P treatment, with P+N and P+N+B treatments having lower Al concentrations in leaching water in both the nine day and 24 hour experiments (Figure 3.9f).
Figure 3.9: Peat, needle and brash column experiments from 24 hour (top panels) and nine day (bottom panels) experiments, comparing concentrations in precipitation, water sampled from peat in the peat only (P), peat + needles (P+N) and peat + needles + brash experiments (P+N+B) and additionally from the needle and brash layers of the P+N+B treatments. Variables measured are (a) DOC, (b) potassium (K), (c) phosphate, (d) ammonium (NH₄⁺), (e) manganese (Mn) and (f) Aluminium (Al). Boxplots show median and interquartile range with means (●). Only the P+N+B experiment had water which remained in the needle and brash layers. Treatments with the same letters were not significantly different. The data
for \( \text{NH}_4^+ \) from the 24 hour experiment could not be modelled using GLMs or GLS, therefore no letters are included.

### 3.4 Discussion

We found that in surface and shallow pore water, DOC, phosphate and K tended to rise post restoration, relative to BOG and FOR controls, with some concentrations subsequently decreasing in surface water by the end of the first growing season. Meanwhile, in deep pore water, restoration trajectories changed comparatively little over time.

One of the key drivers influencing pore water chemistry is water table (Haapalehto et al., 2014), particularly affecting DOC and associated metals (Fenner et al., 2001). The clear increase in WTD following restoration in both ENH and STD plots, occurred from the first post-restoration sampling round (February 15). This showed that tree removal combined with the collector drain blocking was effective in retaining water in the restoration plots. As rewetting occurred quickly from the onset of restoration, this could begin to immediately affect the pore and surface water chemistry (Clark et al., 2012). The rewetting may have been favoured by a very wet autumn and winter (e.g. Figure 3.4b, 470 mm, Oct14-Feb15), therefore management occurring in the spring, followed by a dry summer may not have had the same response.

Following restoration, the greatest deviation from the BOG reference was in shallow and surface pore water, and DOC was one of the water chemistry variables most strongly associated with this trend for each depth. Pore water DOC concentrations have been found to respond strongly to water table changes following restoration in bogs and fens, with some very rapid and large concentration increases occurring (>100%; Fenner et al., 2011; Clark et al., 2012). This was thought to be related to stimulation of microbial processes due to the interplay between phenol oxidase and hydrolase enzymes (Freeman et al., 2001b). Hydrolases degrade simple organic compounds and are constrained by phenolic compounds, whilst phenol oxidases degrade phenolic compounds. Following rewetting, phenol oxidase activity is greatly enhanced by reduction of electron acceptors and labile carbon (C) and nitrogen (N) compounds, allowing inhibitory phenolic compounds to be removed, stimulating intense DOC production by hydrolases (Freeman et al., 2001b; Fenner et al., 2011). Some authors have also attributed the increase in DOC
concentrations upon re-wetting to abiotic processes, such as decreased acidity and enhanced DOC solubility (Chapman et al., 2005; Clark et al., 2012). Therefore, with the rise in water table occurring following forest-to-bog restoration (Fig 3.4c), rewetting stimulated DOC production may have been an important process contributing to the significant increase in DOC concentrations in pore and surface waters.

In addition to the effects of drain blocking, our brash experiment clearly demonstrated the huge potential for brash and needle decomposition to add to the pool of DOC. This has also been observed by Palviainen et al. (2004a) who found mass loss of ≤ 60% of the initial carbon from needles and ≤ 30% from branches during a three-year decomposition experiment. In the present study, the largest increase in DOC concentrations was in ENH plots, although in both surface water and shallow pore water, concentrations decreased by December 2015. Therefore, the extra disturbance caused from additional machinery used in brash removal on ENH plots may have caused a sharper DOC increase (Kiikkilä et al., 2014), but the smaller quantities of brash means that the concentrations also decline sooner. On the other hand, STD plots which had lower peak DOC concentrations, remained steady until December 2015, suggesting decomposition continued into autumn 2015. Our results suggest that mulching may also enhance DOC release, which may be associated with the smaller particle size compared to brash branches, as found by Hyvonen et al. (2000) in a study of logging residue decomposition rates.

While studies of pore water DOC concentrations following re-wetting show increases in the short-term (>1 month; Clark et al., 2012), in the longer term (5-10 years), rewetted sites were found to have lower concentrations than drained sites in the period 5-10 years after drain blocking (Wallage et al., 2006; Haapalehto et al., 2014). Therefore, with a stabilisation of WTD closer to the surface, DOC production can decrease to around that of pristine sites, over a period of 6-20 years (Wallage et al., 2006; Höll et al., 2009).

However, following felling increased DOC concentrations have been found for at least three years (in streams; Niemin nen et al., 2015). Therefore, with the effects of felling, where additional DOC is produced by brash decomposition, combined with those of rewetting, the trajectory for pore and surface water DOC concentrations in future years is less clear. One of the main implications of increased pore and surface water DOC concentrations is increased aquatic carbon export, which can affect the overall carbon balance of the bog (Chapter 5).
3.4.1 Effects of forest-to-bog restoration on variables which are key plant nutrients

The concentrations of K and phosphate also increased more than 3-fold in pore water and more than 8-fold surface water following restoration. Increased K concentration in streams is a well-documented effect of conifer felling (Rosén et al., 1996; Cummins and Farrell, 2003a; Muller et al., 2015). K is known to be released from brash and needle decomposition, which occurs at a greater rate in felled areas than standing forestry (Palviainen et al., 2004a). Increases in phosphate concentrations were also particularly strong in surface water and in shallow pore water. Phosphate is known to be release from brash and in particular decomposing conifer needles (Kaila et al., 2012; Asam et al., 2014a). Our results suggest that mulching may also enhance phosphate release, which may relate to the smaller size of mulch compared to brash, allowing faster growth of decomposers and phosphate release (Hyvonen et al., 2000). In a study of nutrient stoichiometry in peatlands across Ontario, Canada, an increase in the carbon: phosphorus ratio from plants to litter to peat was found, suggesting strong utilisation of phosphate by plants (Wang et al., 2014b), which may be partly by mycorrhizal and root uptake (Turner, 2008; Wang et al., 2014a). Therefore, there is potential for utilisation of the excess phosphate resulting from forest-to-bog restoration.

Ammonium increases were found in shallow pore water and surface water post-restoration. Increased $\text{NH}_4^+$ has been found in surface runoff from brash mats on felled areas, and also in the peat under brash mats (Asam et al., 2014b). Ammonium is produced from the mineralisation of organic N (ammonification; Bowden, 1987) and is a product of brash and needle decomposition (Asam et al., 2014a). In bogs concentrations can be seasonally variable due to uptake from surface water in the growing season (Wieder et al., 1985). In the present study this seasonal pattern was visible in shallow pore water concentrations in June sampling rounds. In deep pore water, FOR plots had the highest $\text{NH}_4^+$ concentrations. This may have been due to (tree) root exudation through active microbial processes during the growing season (Wieder et al., 1985), although $\text{NH}_4^+$ concentrations were high also in winter in deep pore water in FOR plots, suggesting the $\text{NH}_4^+$ was not utilised by microbes or trees.

The observed increases in Mn in surface water is also likely related to brash decomposition. Mn is a plant micronutrient (Millaleo et al., 2010) and is released from needles (Asam et al., 2014a). Increased Mn is known to occur in streams post felling (Cummins and Farrell, 2003a).
In general, for each of the plant nutrients discussed above (K, NH$_4^+$, phosphate and Mn), our column experiments confirmed that significant amounts of these were leached from brash, and phosphate, NH$_4^+$ and Mn were specifically released in the needle layers, which is consistent with other studies (Kaila et al., 2012; Asam et al., 2014a, 2014b).

Concentrations of TON in pore water were lower than NH$_4^+$. This was likely due to a lack of oxygen for complete N mineralisation, which was dominated by ammonification (Bowden, 1987; Andersen et al., 2013b). In bogs methanotrophs can also outcompete nitrifying bacteria, preventing nitrification and production of NO$_2^-$ and NO$_3^-$ (TON; Megmw and Knowles, 1987). These mechanisms can also help explain the lack of TON production in the brash experiments in addition to evidence that N has been found to be accumulate during the early decomposition of conifer needles (Moore et al., 2011; Asam et al., 2014a). TON appeared to be removed from precipitation (leaching solution) when in contact with peat, needles and brash, as precipitation had the highest TON concentrations (data not shown). This is commonly observed with conifers and the amount removed is in proportion to concentrations in precipitation (Nisbet and Evans, 2014).

3.4.1.1 Implications of increased concentrations of plant nutrients

For the water chemistry variables most likely leached from brash and needle decomposition in this study (DOC, K, and phosphate), concentration increases were less pronounced in deep pore water. This may be linked to higher rates of lateral flow than vertical flow in blanket bogs (Holden and Burt, 2003b). Instead, the newly mineralised nutrients may be transported to streams (Asam et al., 2012b), where there could be potential impacts on water quality (Chapter 4). Generally, it has been found that phosphorus (P) is released faster than N from decomposing forest litter (Moore et al., 2011). This may explain why we found larger increases in phosphate than NH$_4^+$ in the first year following restoration. Moore et al. (2011) hypothesised that there may be N accumulation in forest litter (and C release) until a critical C:N ratio is reached, at which N is then lost. Thus, there may be a greater risk of phosphate leaching to streams draining the restoration sites in the short-term (0-1) years but in the medium-long term, there may be N release and leaching to streams.
There are implications of excess plant nutrients in relation to re-colonisation by bog vegetation (Bubier et al., 2007), which is essential for restoring a functional peat accumulating system. Firstly, nutrient co-limitation has been found in bogs (Wang and Moore, 2014), where additions of N, P and K, increased vegetation abundance more than adding N only (Larmola et al., 2013). However, nutrient addition has been widely found to favour vascular plant growth and negatively impact on Sphagnum species (Xing et al., 2011; Larmola et al., 2013). One study found the strongest decrease of Sphagnum when N + P + K were added together (Xing et al., 2011). In another study on fertilisation on bogs, the addition of P+K and N+P+K was found to reduce Sphagnum growth within two years and after four years no Sphagnum growth was observed (Bubier et al., 2007). Similarly, in revegetated constructed fens, high N:P ratios (P limitation) were found to hamper the diversity of the plant community structure, favouring vascular plants over bryophytes (Nwaishi et al., 2016).

These studies imply that an excess of \( \text{NH}_4^+ \), phosphate and K as found in forest-to-bog restoration may not be conducive to the immediate colonisation and growth of typical bog vegetation, in particular Sphagnum mosses e.g. (Hancock et al., in prep.). In the short term vascular plants such as such as Eriophorum spp. (cotton grass), Myrica gale (bog myrtle) and Calluna vulgaris (common heather) may be promoted instead. However, most studies of nutrient addition are looking at the response of bog vegetation on bog sites (Xing et al., 2011; Larmola et al., 2013), while in our study, in the restoration plots ground vegetation was altered by the period of forestry (Table 3.1), thus we have a different starting point prior to nutrient addition. In the longer term (14 years) post-restoration on a formerly drained afforested site, bog vegetation had not completely recovered (in comparison to open bog controls), which may have been in-part due to elevated plant nutrients (Hancock et al., in prep.).

Increased vascular plant abundance following nutrient addition, has been found to reduce the rate of net ecosystem exchange (NEE) of CO\(_2\) due to reduced photosynthesis (Bubier et al., 2007) and increased respiration (Larmola et al., 2013). Reductions in photosynthesis have been associated with nutrient toxicity to Sphagnum mosses, increased vascular plant shading and increased litter production, which in turn reduced NEE, ultimately decreasing the amount of CO\(_2\) being sequestered by the bog over five years (Bubier et al., 2007). Therefore, it is important for restoration to target
re-colonisation by the desired bog species (*Sphagnum*) for both habitat and carbon functions.

### 3.4.2 Effects of forest-to-bog restoration on other water chemistry variables

The increase in pH in surface water following restoration may be related to increased concentrations of base cations (K, Ca, Mg) which act to increase pH, through cation exchange with the peat matrix (Andrews et al., 2003). However, as pH in the BOG sites was significantly higher post-restoration, these changes may also have been influenced by weather. During the pre-restoration period, there were drought periods (summer 2013, 2014), which have been associated with acidification of pore water (Clark et al., 2012) and following restoration, there was more consistent rainfall across the post-restoration period (Figure 3.4b). We also acknowledge that, in this case, the pre-restoration sampling period was also shorter, which may have influenced the statistics.

Other significant increases in concentrations of pore and surface water chemistry variables following forest-to-bog restoration, may be related to the WTD increase and inputs or disturbance of mineral material, rather than brash and needle decomposition. For example, Fe concentrations are well known to be related to water table and redox conditions (Fenner et al., 2001; Muller et al., 2015). In shallow pore water, insoluble Fe (III) in the peat would have been reduced to soluble Fe (II), as peat re-wetted and oxygen was depleted, thus Fe was then an alternative electron acceptor for microbial activity (Küsel et al., 2008). Therefore, this may explain some of the Fe increases in surface and shallow pore water post-restoration. However, association with humic substances (DOC) may also have kept some Fe(III) in solution (Fenner et al., 2001), thus increasing along with DOC concentrations in pore and surface water (significant correlations ≥0.5 in surface and shallow pore water).

Al and Ca increased post-restoration in surface water of ENH and STD plots compared to the reference. Similar increases in Al had been found by Kiikkilä et al. (2014) in surface water (ditches) in some drained afforested (Scots Pine, Norway Spruce) peatland sites where both stem only harvest and whole tree harvest were carried out. In our study, larger Al increases were found in ENH plots than STD, yet there was more brash (and needles) remaining on STD plots. Although there may also be some site specific factors (ENH plots also had slightly higher Al pre-restoration), it appears that increased Al might not
have been leached from needle decomposition as has been found by others (Asam et al., 2014a). In our brash and needle leaching experiments, the highest Al was from the peat layer of the peat only treatment, which supports the above hypothesis.

An alternative source could be the peat itself, releasing Al and Ca following disturbance to underlying mineral soil from restoration machinery (Muller and Tankéré-Muller, 2012). Haapalehto et al. (2014) found that ditches from restored plots tended to have a higher minerogenic influence than pore water, attributing this to ditches being preferential flow paths. This may help explain why increased Al and Ca were only found in surface water (ditches) and not pore water.

Generally, in deep pore water, there were fewer significant increases (and smaller effects) in water chemistry variables post-restoration than in shallow or surface water. Increased conductivity and Mg occurred only in STD plots in deep pore water post-restoration. This suggests an effect of remobilisation in deep peat due to water table changes on Mg and conductivity as a summative measure of all soluble ions (Vogt et al., 2010), affected by remobilisation. Along with DOC, (and Ca) these were the only significant changes in deep pore water (out of the variables we tested; Table 3.2). It appears that deep pore water is less affected by management on the peat surface, compared to shallow pore water or surface water.

3.4.3 Seasonal patterns of pore and surface water chemistry

There was significant temporal variation in water chemistry with up to 35 % of surface water chemistry and 25 % of shallow pore water chemistry explained by the interaction of plot-class and time. DOC was one of the main elements following these temporal changes in both pore and surface waters, along with K, phosphate and conductivity. This was indicated by PRC which enables visualisation of the main variables driving an overall change with time (Poulin et al., 2013; Nwaishi et al., 2016). The trend in surface and shallow porewater showed concentrations increasing post-restoration but also with seasonal differences during this period. Sampling in the post-restoration period was from February 2015. The PRC and time-series for individual water chemistry variables showed that in this first sampling round, most concentrations were similar to pre-restoration levels in winter. Post-restoration increases in concentrations occurred mainly from June 2015 (next sampling after February), suggesting a strong seasonal control on pore and surface water.
water chemistry, where increased concentrations were associated with higher air and pore water temperatures. Summer maxima in concentrations is a common feature of pore and surface water chemistry, related to the evaporation-precipitation balance, increased mineralisation and the balance of plant uptake and exudation (Wieder et al., 1985; Proctor, 2006; Anderson, 2010). Increased plant uptake may cause declines in surface water nutrient concentrations (Wieder et al., 1985), however the increases following restoration, were much larger than the pre-restoration seasonal cycling. Higher temperatures can significantly increase decomposition rates in soil (Chow et al., 2006; Davidson and Janssens, 2006) and furthermore in combination with WTD movements this can increase net mineralisation (DOC production; Clark et al., 2009). In line with this trend, pore water temperature was found to increase slightly (2-3 ºC) in deep and shallow pore water, post-restoration in both ENH and STD plots (data not shown). This may have further increased the potential for nutrient and DOC mineralisation (Koerseliman et al., 1993), helping in part to explain the some of the concentration increases we found. Increased pore water temperature is likely due to increased sunlight exposure post-restoration, as pre-restoration there was shading of the peat surface by forestry.

The PRC showed a trend of moving further away from the BOG reference in the post-restoration period and those variables, which followed this trend. However, being a multivariate method, looking for differences between reference and treatments (van den Brink and Ter Braak, 1999), it also identified variables which were different across the entire study period, as an effect of forestry. These variables showed seasonal patterns but not a clear effect of restoration. For this reason, Na, Ca, Mg and conductivity were identified as high scoring variables but did not show many changes following restoration (when tested with univariate statistic), remaining higher than bog as they were in the pre-restoration period. Thus this is one limitation of using PRC in a BACI design.

### 3.4.4 Implications of management techniques

It was found that ENH fell (harvesting stems and then removing brash) sometimes resulted in greater concentration increases than STD fell. This was true for DOC at all depths and for many other variables in surface water (NH₄⁺, phosphate, Fe, K, Mn, Al, Ca). All of these variables (except NH₄⁺ and Al) then decreased in concentrations by December 2015 to lower than STD fell plots. Therefore, ENH plots had greater concentration increases (in surface water) which appeared shorter lived. There were
features of the ENH treatment which may have contributed to these changes: 1) ENH plots had greater physical disturbance, with more passes by felling/harvesting machinery as the ENH treatment used four different machines, whereas the STD treatment used two. 2) ENH plots on average had a lower WTD than STD, despite both treatments seeing a significant increase post-restoration. Therefore, there was a larger aerobic zone in ENH plots, in which mineralisation of nutrients may have been stimulated by the newly rewetted zone below (Shenker et al., 2005; Borken and Matzner, 2009).

STD fell plots also saw many significant concentration increases in surface water and in shallow pore water, STD plots had higher peak NH$_4^+$, phosphate, Fe, K than ENH plots. These plots did not also show the same decreases by December 2015, perhaps as there was such an excess of nutrients left from summer season, rather than mineralisation continuing into the winter e.g. (Kieckbusch and Schrautzer, 2007). These patterns suggest that in STD plots there may be a slower release from leftover brash, which leaches to shallow pore water. It would be expected that STD plots, may become a slower source of nutrients over the period in which brash decomposes (0-12 years: Moore et al., 2011). Furthermore, the presence of brash mats on STD plots may also prevent bog vegetation recovery on the peat surface below.

The limited number of MUL plots sampled also suggests that mulching may enhance the release of DOC, phosphate and K in surface water and shallow porewater. Other studies have found mulch to leach nutrients to soil three-five years after treatment (Rhoades et al., 2012). However, in our study mulching was not considered a stand-alone restoration treatment, but used on crop failure areas within the STD and ENH felling treatments.

At the present time, it is difficult to conclude whether STD or ENH treatments are a better restoration method in terms of the effects on pore and surface water quality. It is clear from the column experiments that brash and needles are a source of many of the water quality variables measured in this study and are therefore a key control on pore and surface water chemistry. In the longer term, removing brash from plots would appear a useful measure to mitigate against high concentrations of nutrients in pore and surface water. However, a longer period of monitoring would be necessary to monitor future concentration changes over time, to determine whether STD plots do show increased concentrations extending over a longer period, due to the remaining brash. This would also determine whether ENH plots show similarly high peaks in surface water concentrations in the following summer seasons and whether the extra disturbance in
ENH plots to remove this brash is a benefit in the longer term. As ENH plots also showed higher concentrations of elements associated with mineral inputs (Al, Ca, Mg), it would be interesting to monitor these over a longer period and in streams and rivers (Chapter 4), e.g. as Al concentrations are toxic to Atlantic Salmon (Kroglund and Finstad, 2003).

3.5 Conclusion

Our results showed significant increases in concentrations of DOC, phosphate, K and NH$_4^+$ in surface water and shallow porewater post-restoration, in ENH and STD plots relative to BOG and FOR controls. These increases occurred from the first summer following restoration (June 2015), which was carried out the previous winter or spring. There were indications of a decrease in some variables by the end of first year post-restoration (December 2015), although concentrations remained elevated above pre-restoration levels. Meanwhile, in deep pore water, restoration trajectories changed comparatively little over time, with smaller increases in DOC, Mg and conductivity. We also found significant increases in WTD post-restoration in both ENH and STD plots relative to controls.

At present, after one year of post-restoration monitoring, we cannot determine the best restoration method due to the different responses of STD and ENH treatments, in surface and porewater chemistry. The sharper and larger increases in DOC, plant nutrients and metals (Ca, Al, Fe) which occurred in surface water within the ENH plots, declined by December 2015. This suggest enhanced felling (stem plus brash harvesting) may have a lesser impact on water chemistry over longer time periods, but it would be necessary to determine whether ENH plots show similarly high peaks in surface water concentrations in subsequent summer seasons. Similarly, we suspect that the slower response in STD plots, may show continued increases in surface and pore water concentrations, as brash continues to slowly decompose, although this also may be influenced by seasonal patterns. We propose future monitoring of plant nutrients (NH$_4^+$, phosphate, K), DOC and WTD in surface and shallow pore water in the coming 2-5 years, along with surface vegetation, to assess recovery to bog conditions in the medium term and guide future restoration management of afforested blanket bog.
4. Stream and river water quality in the first year following forest-to-bog restoration

4.1 Introduction

Across the world, peatland rivers and streams are important sources of dissolved organic carbon (DOC) and associated metals to the oceans. As such, they help to regulate and maintain global oceanic nutrient cycling, through the delivery of iron required by primary producers (Krachler et al., 2010) and organic matter (DOC) as a food source for heterotrophs (Amon and Benner, 1996). Furthermore, peatland rivers provide a number of other key societal services (Bain et al., 2011). For example, in the UK, rivers draining blanket bog peatlands support large populations of Atlantic Salmon (Salmo salar; Youngson et al., 2002) and provide drinking water (Evans et al., 2005).

Stream and river water quality is affected by both natural and anthropogenic processes occurring over a range of timescales. For example, the delivery and stream concentrations of various elements are affected by seasonal changes and variations in hydrological conditions. DOC is a by-product of decomposition (Neff and Asner, 2001; Bengtson and Bengtsson, 2007), and increases in summer when microbial activity peaks (Davidson and Janssens, 2006; Dinsmore et al., 2013). It is delivered to streams from surface run-off and porewater and increases during storm events (Koehler et al., 2009). Contrastingly, calcium (Ca) concentration is controlled by the influence of groundwater on stream chemistry and thus tends to increase during low flow conditions (Worrall et al., 2003). Other elements depends on conditions in the peat itself: for example, iron (Fe) concentration and mobility changes with the evaporation-precipitation balance controlling redox conditions within the peat (Küsel et al., 2008; Muller and Tankéré-Muller, 2012).

In addition to these natural sources of variation, land management operations which cause a physical disturbance such as tree-felling or manipulation of the water table can impact upon stream water chemistry (Wilson et al., 2011a; Finnegan et al., 2014b) and have been found to negatively impact water quality (Neal and Reynolds, 1998). This may include forest-to-bog restoration, a land-use change that is currently being implemented widely across Western Europe (Andersen et al., 2016; Anderson et al., 2016).
Despite restoration (including conifer removal) being carried out over the past 20 years in many areas including Northern Scotland, Northern Ireland, England, Switzerland and France, there is little published research on its impact on water quality (Andersen et al. 2016). Recent work has shown impacts of forest-to-bog restoration on stream chemistry, more specifically on DOC, aluminium (Al), potassium (K) and phosphorus (P) within close proximity to management (Muller et al., 2015). The wider body of research on forest felling further demonstrates that forest-to-bog management could disrupt the current biogeochemical cycling and fluvial transport of carbon, nutrients and metals, with the potential to impact on stream ecology (Neal et al., 2004; Asam et al., 2014b; Finnegan et al., 2014b; Kaila et al., 2014). Forest-to-bog restoration is increasingly being practiced on afforested areas of deep peat (>50cm) to protect carbon stocks (Morison et al., 2010; Morison, 2013) and re-create protected blanket bog habitat (Bain et al., 2011). Overall, approximately 11% of the Scottish afforested area (Morison et al., 2010) could be targeted by restoration in the coming decades. Understanding the impact of this rapid and widespread land-use change on water quality is therefore timely and critical.

4.1.1 The effects of conifer felling on water quality and mitigation measures

In forest streams, increased concentrations and exports of DOC, nutrients and metals have been measured in the years after felling (Finnegan et al., 2014b; Kiikkilä et al., 2014; Nieminen et al., 2015). These effects have been found to last for at least two to four years post felling (Cummins and Farrell, 2003b; Nieminen, 2004). Phosphorus is commonly added as fertiliser in afforested peatlands (Cummins and Farrell, 2003a) which is then released when brash left on site decomposes (Palviainen et al., 2004a). Increased stream P post-felling (Rodgers et al., 2010) is particularly significant as P is often the limiting nutrient for freshwater eutrophication (Hecky and Kilham, 1988), which can cause loss of fish and macroinvertebrate species (Weijters et al., 2009). As nitrogen is often not limiting, algal blooms can respond in proportion to P additions (Smith and Schindler, 2009).

The delivery of metals from felled peatlands into streams can also cause ecological problems. Firstly, elevated concentrations of dissolved Al are toxic to salmon at early (freshwater) developmental stages (Buckler et al., 1995) and smoltification (physiological changes prior to first migration to sea), causing impaired gill enzyme activities and
mortality (Kroglund et al., 1999). Secondly, as metals are removed from the soil in harvested timber, a lack of base cations can reduce the buffering capacity of soils and streams (Nisbet and Evans, 2014). This leaves fish and aquatic organisms more vulnerable to acidic episodes (Likens, 2013).

To help minimise the impacts of conifer felling, the use of buffer strips (10-30m wide unfelled strips of standing forest adjacent to the stream) has been effective in preventing the leaching of nutrients and suspended particulate matter (SPM; Ahtiainen and Huttunen, 1999; Löfgren et al., 2009). Although the use of riparian buffer zones planted with broadleaved trees has been recommended as a more effective practice in Scottish and Irish forestry (Forestry Commission, 2011; Finnegan et al., 2012). Another factor which can dictate the impact of felling on water quality is the proportion of a catchment which is felled (Neal and Reynolds, 1998), but evidence regarding this is inconsistent across regions. For example, in East Finland felling 12% of a catchment increased SPM export, while felling 34% also increased nitrogen (N) and P exports (Palviainen et al., 2014). However, clear felling 40% of a catchment in Western Scotland over a four year period did not affect water clarity or colour (Nisbet et al., 2002). Therefore, there are likely to be catchment specific factors which affect water quality and no clear evidence-based guidance is available for restoration of UK afforested peatlands.

4.1.2 The effects of drain blocking on water quality

As well as tree removal, forest-to-bog restoration often includes drain blocking, which is intended to raise the water table and restore the habitat by retaining water within the restoration area (Holden et al., 2007b; Parry et al., 2014). This can also have an impact on stream water chemistry. Rewetting of both open bogs and fens across the UK, led to increased concentrations of metals and DOC in porewater (Fenner et al., 2001, 2011; Clark et al., 2012). Porewater changes can be closely linked with stream concentrations (Billett et al., 2006), although changes in small scale watercourses (drains) are not always detected in larger streams (Worrall et al., 2007). So far, studies evaluating the effects of drain blocking have mainly focussed on pore water chemistry or aquatic carbon export in streams (Wilson et al., 2011a; Parry et al., 2014), and have rarely included the combination of drain blocking and tree removal. Therefore, there is a gap in
understanding regarding the impacts of drain blocking on stream water quality in the context of forest-to-bog restoration.

4.1.3 Chapter aims

Given the scale of peatland restoration targets in Scotland and the UK (Bain et al., 2011) and the socio-economic importance of freshwater systems that take their source in those peatlands (Butler et al., 2009; Martin-Ortega et al., 2014), it is critical to gain a better understanding of the short-term impacts of the combined effects of felling and drain blocking on the water quality of receiving streams and rivers. Thus, the aim of this chapter was three-fold: 1) to determine the effect of forest-to-bog restoration management on the water quality of streams and receiving rivers in the first 15 months following felling; compared to 15 months pre-felling, 2) to investigate the influence of seasonality and hydrological conditions on water quality, and how they related to forest-to-bog restoration and (3) to assess the possible impacts of water quality changes on the stream and river ecosystem in terms of UK statutory water quality standards. It was hypothesised that water quality changes would be greater in streams than in rivers. In particular, we hypothesized that there would be measurable increases in concentrations of DOC, nutrients and metals within the first 15 months. We also hypothesized that the natural seasonal signals in water quality would be stronger (larger amplitude of variation) in streams impacted by forest-to-bog restoration than in their natural counterparts.
4.2 Methodology

4.2.1 Site description

Forest-to-bog restoration in the Dyke Forest, RSPB Forsinard Flows National Nature Reserve commenced in October 2014 over seven restoration sites (Chapter 2.2). These sites were all within the catchment of the River Dyke or Halladale (Figure 4.1). The River Dyke is the major river which receives drainage from most of the Dyke Forest. It is 13 km long, with a catchment of 57km², and is sourced from waters arising on the open slopes of Ben Griam Beg and adjacent bogs (Vinjili, 2012).

The River Dyke drains an area of private plantation forestry, then flows through open bog and receives drainage from previously restored areas (Cross Lochs, restored 2005-2006) before entering the Dyke Forest (originally state owned). It joins the Halladale River just south of Trantlemore on the A897 (Figure 4.1). The River Halladale is a privately owned salmon fishing river, managed by the Strath Halladale partnership. It is 29 km long, with a catchment area of 267 km² (Vinjili, 2012), which is mostly peat covered (Lindsay et al., 1988), with the River Dyke making up about 20% of its catchment.

4.2.2 Stream water sampling and hydrological measures

The sampling strategy targeted streams directly receiving drainage from restoration sites and the rivers these streams drained into. Four first, or second order streams draining restoration sites (DK2, DK4, DK5, DK6) were selected for monitoring of stream water quality, which were termed restoration streams (Figure 4.1/ Table 4.1). In restoration streams, samples were taken both upstream of the restoration site (afforested control point) and downstream of the restoration (treatment). Additional controls included one afforested (“negative”) and two open bog (“positive”) streams, which were in catchments unaffected by forest-to-bog restoration management (Figure 4.1). These streams only had one sampling point each. The River Dyke was sampled upstream and downstream of the confluence with adjoining restoration streams, while in the River Halladale this included upstream and downstream of the River Dyke confluence. In total, 20 points were sampled monthly from May 2013 to December 2015 except during the main felling and mulching period (October to December 2014), when samples were taken fortnightly to better capture any immediate changes in water quality.
Figure 4.1: (a) Stream and river sampling map: Orange plots show where drainage streams were monitored, blue plots show other restoration areas within the Dyke catchment and yellow squares show discharge monitoring sites. (b) Schematic of stream and river sampling design for Dyke Forest restoration plots and control streams. (c) Schematic of bog control and afforested control catchment sampling points, green panel is the area shown in panel (b). The colour coded key refers to the five classes of sample points (panels b,c): green = bog stream control sites (BOG), grey = forest streams control sites (FOR), yellow = restoration treatment stream sites (REST), blue = river baseline sites (BASE-R) and dark red = restoration treatment river sites (REST-R). Class refers to treatment of data for averaging and statistical analysis and reflects the sampling location rather than the whole upstream catchment. Note that baseline river sites (BASE-R) are upstream of treatment sites (REST-R) but both are on the same rivers. This sampling strategy also applies to FOR sites, which are upstream of REST (stream) sites but there is also an independent forest control stream included in this class (site 16). There was no upstream FOR control site on the restoration stream from DK5, as the stream was sourced from within the DK5 restoration area.

Two samples were collected at each sampling point (250 mL for chemical analysis and 500 mL for SPM) in HDPE bottles (Nalgene) rinsed twice with sample water and kept in a cool box until their return to the laboratory. Samples were refrigerated at 4°C on return to the laboratory and filtered normally within 24 hours of collection (always within 36 hours) as described in Chapter 2.5.1. They were then analysed for concentrations of DOC, DIC, NH$_4^+$, NO$_3^-$, soluble reactive phosphate (SRP) and a suite of macro (Ca, K, Mg, Na, S) and trace elements (Al, Cu, Fe, Mn, Ni, Zn; Chapter 2.51). DOC quality was also measured by absorbance (Chapter 2.5.1). Additional chemical analyses performed on stream and river water samples are described in the following sections. Stream discharge was logged continuously at sites 11 (restoration treatment stream), 16 (forest control stream) and 19 (bog control stream) (see chapter 5.2 for details).
Table 4.1: Stream and river sampling site descriptors. Class refers to grouping of sample points for statistical analysis is also used in Figure 4.1: bog stream control sites (BOG), forest streams control sites (FOR), restoration treatment stream sites (REST), river baseline sites (BASE-R) and restoration treatment river sites (REST-R). Note that BASE-R sites (are not independent of the REST-R sites and some FOR sites, are not independent of the REST (stream) sites. See Figure 4.1 for details.

<table>
<thead>
<tr>
<th>Site</th>
<th>name</th>
<th>class</th>
<th>Stream order</th>
<th>Catchment area (ha)</th>
<th>Land use</th>
<th>Sampling location</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DK2 stream (baseline)</td>
<td>FOR</td>
<td>1</td>
<td>30</td>
<td>Mainly afforested, 8% undergoing restoration (2.4 ha)</td>
<td>NC 86129 48262</td>
</tr>
<tr>
<td>2</td>
<td>DK2 stream (treatment)</td>
<td>REST</td>
<td>1</td>
<td></td>
<td></td>
<td>NC 85903 48377</td>
</tr>
<tr>
<td>3a</td>
<td>R. Dyke (baseline)</td>
<td>BASE-R</td>
<td>4</td>
<td>see 14</td>
<td>see 14</td>
<td>NC 85751 47943</td>
</tr>
<tr>
<td>3</td>
<td>R. Dyke (DK2)</td>
<td>REST-R</td>
<td>4</td>
<td></td>
<td></td>
<td>NC 85888 48355</td>
</tr>
<tr>
<td>4</td>
<td>R. Dyke (DK2)</td>
<td>REST-R</td>
<td>4</td>
<td></td>
<td></td>
<td>NC 85881 48432</td>
</tr>
<tr>
<td>5</td>
<td>DK4 stream (baseline)</td>
<td>REST</td>
<td>2</td>
<td>120</td>
<td>54% open bog (upper catchment), 43% afforested, 3% undergoing restoration (3.6 ha)</td>
<td>NC 85201 50286</td>
</tr>
<tr>
<td>6</td>
<td>DK4 stream (treatment)</td>
<td>REST</td>
<td>2</td>
<td></td>
<td></td>
<td>NC 85971 49962</td>
</tr>
<tr>
<td>7</td>
<td>R. Dyke (DK4)</td>
<td>REST-R</td>
<td>4</td>
<td>see 14</td>
<td>see 14</td>
<td>NC 86705 49827</td>
</tr>
<tr>
<td>8</td>
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<td>REST-R</td>
<td>4</td>
<td></td>
<td></td>
<td>NC 86740 49872</td>
</tr>
<tr>
<td>9</td>
<td>DK5 stream (treatment) / DK 6 stream (baseline)</td>
<td>REST</td>
<td>1</td>
<td>133</td>
<td>Mainly afforested, 23% undergoing restoration (30.6 ha)</td>
<td>NC 88097 48756</td>
</tr>
<tr>
<td>10</td>
<td>DK 5/6 stream (treatment)</td>
<td>REST</td>
<td>1</td>
<td></td>
<td></td>
<td>NC 88037 49463</td>
</tr>
<tr>
<td>11</td>
<td>DK 5/6 stream (treatment, downstream)</td>
<td>REST</td>
<td>3</td>
<td>412</td>
<td>40% of catchment afforested (upper catchment), 12% undergoing restoration (49.7 ha), 48% open bog (lower catchment)</td>
<td>NC 89373 51248</td>
</tr>
<tr>
<td>12</td>
<td>R. Halladale (baseline)</td>
<td>BASE-R</td>
<td>5</td>
<td>see 15</td>
<td>see 15</td>
<td>NC 89593 51043</td>
</tr>
<tr>
<td>13</td>
<td>R. Halladale (DK5/6)</td>
<td>REST-R</td>
<td>5</td>
<td></td>
<td></td>
<td>NC 89566 52093</td>
</tr>
<tr>
<td>14</td>
<td>R. Dyke (mouth)</td>
<td>REST-R</td>
<td>4</td>
<td>5717</td>
<td>Mixture of afforested open bog and undergoing restoration (3% in this study; 174 ha)</td>
<td>NC 89577 52308</td>
</tr>
<tr>
<td>15</td>
<td>R. Halladale (R. Dyke)</td>
<td>REST-R</td>
<td>5</td>
<td>10075</td>
<td>Mixture of afforested, open bog and undergoing restoration.</td>
<td>NC 89577 52308</td>
</tr>
</tbody>
</table>
### 4.2.3 Suspended particulate matter (SPM), particulate organic carbon (POC) and turbidity

SPM and POC were both determined gravimetrically by filtration through pre-treated and pre-weighed 0.7 µm glass fibre filters (Fisherbrand MF300) under vacuum, using a Millipore glass filtration unit. Filters were first pre-treated by filtering 100 mL of Milli-Q water, followed by oven drying at 105°C and ashing at 450°C (6 hr) in a muffle furnace. Approximately 500 mL of sample was filtered. Filters were then oven dried (105°C, 12 hours) to remove moisture and then cooled in a desiccator before being re-weighed to determine SPM in mg L⁻¹. The filter was then ashed in a muffle furnace (375°C, 16 hours; Hope et al., 1997; Dawson et al., 2002), desiccator cooled and re-weighed to give loss on ignition (LOI). Ashing at 375°C oxidises most carbonaceous material and is known to provide an accurate estimate of organic matter in soils (Keeling, 1962; Ball, 1964). POC was calculated using the regression equation developed by Ball (1964) for non-calcareous soils to convert LOI at 375°C to POC (Hope et al., 1997a; Dawson et al., 2002):

\[
Y = 0.458 \times X - 0.4
\]  

[Equation 4.1]

where \(Y\) was organic carbon (%) and \(X\) was the LOI (%). \(Y\) was then multiplied by LOI (in mg L⁻¹) to calculate POC in mg L⁻¹. For both SPM and POC determination, blank filters were used (having filtered 200 mL of Milli-Q water) to correct for any mass losses from filters during the process.
A second measure of particulate matter (accounting for very fine particulates not retained by filtration) was made on samples using a turbidity meter (Lovibond, Turbicheck; e.g. Gippel, 1995), which measured the scattering of light at 90º by suspended particulates. This gave a measure in nephelometric turbidity units (NTU). The instrument calibration was checked with known turbidity standards prior to use.

### 4.2.4 Acid Neutralising Capacity (ANC) and Gran alkalinity

Acid neutralising capacity (ANC) is a measure of acidity, linearly related to alkalinity and non-linearly related to pH. It is used in environmental assessment as it is robust (behaving conservatively on mixing) and is unaffected by CO₂ degassing, Al or Al-organic precipitation (Neal et al., 1999). ANC is defined as the sum of the strong base cations minus the sum of the strong acid anions (Neal et al., 1992, 1999). It can also be reliably estimated using measurements of Gran alkalinity, total dissolved Al and DOC (Neal and Reynolds, 1998):

\[
ANC_{est} = Gran\ Alkalinity - 3 \times [Al] + 0.054 \times [DOC]
\]  
Equation 4.2

where [Al] is the concentration of Al in µmol L\(^{-1}\) and [DOC] is the concentration of DOC in µmol L\(^{-1}\). As Al and DOC were measured routinely on stream samples, only Gran alkalinity was required (in addition) to calculate ANC. Alkalinity is a measure of anion species formed from weak acids (pK\(_a\) > 4), made up mainly of bicarbonate (HCO\(_3^\)\(^-\)) and at lower pH, DOC and aluminium species, which counter-act acidity. Using the Gran method (Gran, 1952), titrating to pH 4-5 determined the bicarbonate component while titration below pH 4 accounted for the organic acid contribution (Neal et al., 1999). To measure Gran alkalinity, samples were titrated with 0.001 M HCl to an end point of 3.5. The slope of the change in hydrogen ion concentration versus the volume of acid added was used to calculate the Gran alkalinity in µEq L\(^{-1}\) (Neal, 2001). The exact strength of the acid used was first determined by titrating a 20 mEq L\(^{-1}\) standard made of Na\(_2\)CO\(_3\). Titrations were performed manually using a burette, a pH meter (Jennway 3345 Ion Meter) and a magnetic stirrer.
4.2.5 Statistical analyses

All statistical analyses were performed using RStudio (Version 0.98.501, R Core Team, 2016). All sample points were assigned the class referred to in Figure 4.1. The five watercourse classes were, bog stream control sites (BOG, n=2), forest stream control sites (FOR, n=3), restoration treatment stream sites (REST, n=6), river baseline sites (BASE-R, n=2) and restoration treatment river sites (REST-R, n=7). The BASE-R sites were upstream of REST-R sites. As both were on the same rivers, they are therefore not independent of each other. This sampling strategy also applied to FOR sites, two of which are upstream of REST (stream) sites but here an independent forest control stream was also included in this class (site 16). In addition, the dataset was broken into pre-restoration (December 2013 to October 2014) and post-restoration (October 2014 to December 2015) periods. The pre restoration period ended with the start of forest-to-bog management. The post-restoration thus includes both the period of forest-to-bog restoration (October 2014 – August 2015) and the following months until the end of sampling in December 2015.

To look at the changes in water chemistry of the watercourse classes over time, we used Principal Response Curves (PRC; package vegan, Oksanen et al., 2016), which allowed all classes to be compared to a chosen reference (van den Brink and Ter Braak, 1998, 1999), in our case the bog stream control sites (BOG). This multivariate method specifically tests the time by treatment interaction for a response matrix (log_{10}(x+1) transformed water chemistry), enabling the visualisation of temporal trends in a given class in relation to the reference set (Andersen et al., 2010). Temporal trends are visualised as deviations from the reference rather than absolute values, with each class represented by a response curve. In addition, as this method is based on a redundancy analysis (RDA), it displays the strength of the different response variables with these temporal trends (van den Brink and Ter Braak, 1999). The significance of the principal response curves was tested using Monte Carlo permutations (n=999).

The PRC analysis was used to assess which water chemistry variables differed most from the bog reference over time. Variables which scored strongly (< -0.5 or > +0.5; van den Brink and Ter Braak, 1999) were tested using univariate statistics to look for significant effects of restoration on concentrations in the (restoration) treatments relative to controls. The PRC suggested that some of the key water chemistry variables we hypothesised to be affected by restoration should be tested, but not phosphate or Al. As these are key water quality variables in mandatory water quality standards (EU WFD, UK drinking
water), and for Salmonids (Kroglund et al., 2008; DWI, 2010; European Commission, 2010) we included them in our univariate analyses.

Univariate statistical analysis was carried out at the class level using linear and generalised linear mixed models (LMMs and GLMMs) with the functions *lme* (package *nlme*, Pinheiro et al., 2016) and *glmmpql* (package *MASS*, Venables and Ripley, 2002) to test the effects of time and management. As a simpler (linear) model structure LMMs were first used; where data could not be modelled using LMMs (poor model fit), they were modelled using GLMMs by varying the error family and link functions until the best model fit was found (Thomas et al., 2013). Class (BOG, FOR, REST, BASE-R and REST-R), restoration period (pre- and post-restoration) and the interaction term class*restoration were fixed factors. To account for repeated measures over time we introduced a correlation structure; either a compound symmetry structure for each sampling season (e.g. summer 2013) or a first order autoregressive structure (where successive observations are more correlated than those further apart in time), or an autoregressive-moving-average correlation (depending on best model fit). “Site” was added as a random intercept as sampling sites within each watercourse class had different chemistry and were not assumed to have the same starting point. The best fit models were selected by visually checking normality and homoscedasticity of residuals (Crawley, 2007), autocorrelation of residuals (Zuur et al., 2011) and by the lowest Akaike’s Information criterion (AICc) value (Thomas et al., 2013). Data were transformed log_{10}(x+1) prior to modelling to obtain a more normal distribution, if this improved model fit.

Wald chi-square tests (function *Anova*, package *car*, Fox and Weisberg, 2011) of the model fixed effects were carried out to determine if the interaction term was significant. Thus we used primarily the treatment*period interaction to test for a difference in treatments, relative to that of FOR and BOG controls (i.e. an effect of restoration). If the interaction was significant we used *a posteriori* comparison using least squares means (function *lsmeans*, package *lsmeans*, Lenth, 2016), to test for significant differences between classes (treatments) in the pre- and post- restoration periods.

Data for phosphate could not be modelled using LMMs or GLMMs due to heteroscedasticity of variance. Phosphate was modelled using a generalised least squares model (GLS) using function *gls* (package *nlme*, Pinheiro et al., 2016), following the same
procedure as above. This heterogeneous variance model allowed the variance structure to be specified, by accounting for variation within each level of the factors “class” and “fell”.

To assess the consequences of the effects of forest-to-bog restoration on water quality, observed concentrations were compared in pre- and post-restoration periods to two water quality monitoring frameworks: 1) EU Water Framework Directive (WFD) standards for Scottish rivers and 2) UK standards for drinking water. The EU WFD is designed to protect natural ecosystems, biodiversity and human health (European Commission, 2010), while drinking water standards are designed to protect human consumer health (DWI, 2010). As well as contextualising the results against mandatory water quality regulations, this step helped assess the potential impact of forest-to-bog restoration on the lotic ecosystem.

For every sample collected, parameter concentrations were given a pass or fail status in relation to water quality standards. Percentage pass rates were calculated and grouped by class in the pre- and post-restoration periods respectively. For the WFD, standards are given only for concentrations in rivers; it may have been misleading to compare water quality in small streams to river based standards (i.e., pass rates were only calculated for river classes (BASE-R and REST-R) for WFD standards). The WFD classifies some parameters as a range of four levels from “high” to “poor” depending on concentrations (The Scottish Government, 2014). For these, the percentage of times within each level was calculated. For other parameters, which only have a level for “good” quality, the percentage pass or fail rate was calculated. Metals which appear in the WFD are given as bioavailable concentrations. This is the fraction of a metal responsible for toxic effects in flora and fauna (UK TAG, 2014a). Bioavailable concentrations of a metal are dependent on other parameters (i.e., DOC, pH, Ca; UK TAG, 2014a) and can be calculated using these parameters and the total dissolved concentrations of the metal of interest, using the UKTAG Metal Bioavailability Assessment Tool (UK TAG, 2014b). Bioavailable concentrations of Cu, Zn, Mn and Ni were therefore calculated and percentage pass rates against WFD standards were presented (The Scottish Government, 2014).

For drinking water standards percentage pass rates were calculated for all classes, although only the River Halladale may be used as a drinking water source. These standards are given as single concentrations which define the pass or fail status (DWI, 2010). Statistical differences in pass rates for the WFD and UK drinking water standards were assessed between the relevant classes pre- and post- restoration. This allowed testing
whether forest-to-bog restoration significantly affected pass rates. For WFD standards with levels (high, good, moderate, poor) percentage pass rates for the “high” level only were used in models i.e., pass – exceed “high” level or “fail” to meet high level. As each sample collected had a pass (1) or fail (0) status, this allowed the use of a binomial GLMM for each parameter (Zuur et al., 2011). GLMMs were used with the function `glmer` (package `lme4`, Bates et al., 2015) with the “binomial” family, following the same protocol for concentration data.
4.3 Results

4.3.1 Overall patterns of spatio-temporal change in water chemistry
Temporal patterns in water chemistry differed significantly between the reference stream sites (bog control; BOG) and the afforested and restoration streams and rivers (F=257.3, p=0.001; Figure 4.2) The differences between the reference stream sites (BOG) and the other watercourse classes was greatest during the summer and autumn of 2015 in the post-restoration period, but even in the pre-restoration period, seasonal decoupling was observed.

Figure 4.2: Principal response curves for water chemistry. The left side of the figure represents overall deviation from the reference bog stream control sites (BOG), for the other watercourse classes (forest streams control sites (FOR), restoration treatment stream sites (REST), river baseline sites (BASE-R) and restoration treatment river sites (REST-R)). This is expressed as a canonical coefficient on the first principal component axis (PC1), in comparison with the reference bog stream control sites – represented by the zero line. The right hand side of the figure shows canonical coefficients for all the elements interpreted. A more positive the coefficient showed a stronger relationship with the curve while a more negative coefficient suggests the opposite trend to the curve. The water chemistry parameters most strongly associated with the curves are therefore those, with the highest and lowest coefficients (green shading) e.g. SPM, turbidity and POC follow the trends in the

Sep 13
Jan 15
Oct 14
Feb 14
Jul 14
Jul 15
Nov 15
0.5 threshold
main figure most closely as they were the highest scoring variables. 0.5 was used as the threshold to denote the main water chemistry parameters driving the trend (green broken line and arrow), with parameters scoring >0.5 or <-0.5 analysed with univariate statistics (section 3.2.7). The grey panel shows the period when forest-to-bog restoration management was occurring.

In contrast, during the winter and spring months, the difference between the bog control reference sites and all the other classes was much smaller, and relatively constant. The PRC analysis suggests that in the restoration streams, SPM, turbidity, POC, DOC and Fe increased relative to the bog streams following forest-to-bog restoration, peaking in the summer (2015) and decreasing again towards winter. This was not seen in the rivers, which had lower SPM and DOC than the bog stream and instead, had slightly higher temperature, pH and DIC in the summer months each year, with no obvious changes following restoration.

**4.3.2 Main effects of restoration**

We found significant increases in concentrations of Fe, phosphate and Al following forest-to-bog restoration, relative to the controls (Table 4.1). Despite showing high positive values on the PRC, no significant effects of restoration were found for DOC, POC, SPM or turbidity.
Table 4.2: Summary of significant changes in water chemistry following forest-to-bog restoration, using mixed models. Wald chi-square tests of the model fixed effects were carried out to determine if the interaction term was significant. Thus we used primarily the treatment*period interaction to test for an effect of restoration. If significant (marked in bold), these were followed by Tukey pairwise comparisons (function lsmeans), where letters (CLDs) were derived. Treatments with the same letters were not significantly different. We could not compute letters for phosphate, although a significant effect of restoration was found. Concentrations are means ± SE for each class (bog stream control sites (BOG; n=2), forest streams control sites (FOR; n=3), restoration treatment stream sites (REST; n=6), river baseline sites (BASE-R; n=2) and restoration treatment river sites (REST-R; n=7)), in pre- and post-restoration periods respectively. Phosphate has been abbreviated to Phos, turbidity to conductivity.

<table>
<thead>
<tr>
<th>Interaction</th>
<th>X</th>
<th>p</th>
<th>BOG</th>
<th>FOR</th>
<th>REST</th>
<th>BASE-R</th>
<th>REST-R</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>pre</td>
<td>post</td>
<td>pre</td>
<td>post</td>
<td>pre</td>
</tr>
<tr>
<td>Phos (mg P L⁻¹)</td>
<td>21.90</td>
<td>0.0002</td>
<td>0.001 ± 0.000</td>
<td>0.004 ± 0.003</td>
<td>0.010 ± 0.001</td>
<td>0.007 ± 0.001</td>
<td>0.020 ± 0.002</td>
</tr>
<tr>
<td>Al (mg L⁻¹)</td>
<td>10.09</td>
<td>0.0389</td>
<td>0.034 ± 0.005</td>
<td>0.034 ± 0.008</td>
<td>0.147 ± 0.020</td>
<td>0.190 ± 0.031</td>
<td>0.129 ± 0.012</td>
</tr>
<tr>
<td>Fe (mg L⁻¹)</td>
<td>12.76</td>
<td>0.0125</td>
<td>0.816 ± 0.100</td>
<td>0.718 ± 0.147</td>
<td>0.940 ± 0.075</td>
<td>0.942 ± 0.091</td>
<td>1.597 ± 0.100</td>
</tr>
<tr>
<td>DOC (mg L⁻¹)</td>
<td>3.68</td>
<td>0.4505</td>
<td>13.85 ± 1.37</td>
<td>12.97 ± 1.01</td>
<td>25.06 ± 1.87</td>
<td>25.53 ± 2.17</td>
<td>28.06 ± 1.07</td>
</tr>
<tr>
<td>POC (mg L⁻¹)</td>
<td>6.26</td>
<td>0.1808</td>
<td>1.02 ± 0.30</td>
<td>0.78 ± 0.17</td>
<td>0.88 ± 0.13</td>
<td>1.59 ± 0.53</td>
<td>1.48 ± 0.24</td>
</tr>
<tr>
<td>SPM (mg L⁻¹)</td>
<td>0.38</td>
<td>0.9839</td>
<td>3.38 ± 1.05</td>
<td>2.35 ± 0.49</td>
<td>2.68 ± 0.36</td>
<td>6.09 ± 3.03</td>
<td>5.93 ± 1.08</td>
</tr>
<tr>
<td>Turb NTU</td>
<td>6.30</td>
<td>0.1776</td>
<td>2.87 ± 0.71</td>
<td>2.54 ± 0.46</td>
<td>2.65 ± 0.38</td>
<td>2.78 ± 0.62</td>
<td>6.85 ± 1.05</td>
</tr>
</tbody>
</table>
4.3.3 Temporal effects of restoration on water quality parameters

Across the whole study Fe, DOC, K, Mn, and turbidity reached maximum concentrations during summer months in all stream classes (Figure 4.3). In rivers, this pattern was also observed, although the seasonal concentration differences were smaller. The same trend in streams was also exhibited by phosphate but to a lesser extent.

For each of these parameters in streams, the seasonal increases in summer 2015 (post-restoration) were notably larger than in pre-restoration summers, relative to the BOG and FOR controls. Both Fe and phosphate increased significantly following restoration in treatment classes relative to controls (X=12.76, p=0.0125 and X=21.90, p=0.0002) respectively. This was exhibited as 1.5- and 4.4-fold increases respectively, in mean post-restoration concentrations in REST (stream) sites, compared to their mean pre-restoration concentrations (Figure 4.3a-d).

Although not statistically significant (DOC, turbidity) or statistically tested (K, Mn), very similar temporal patterns were observed for these parameters, with mean post-restoration DOC concentrations increasing 1.3-fold, K increasing 1.9-fold, Mn increasing 2.0-fold and turbidity increasing 1.9-fold, compared to mean pre-restoration increases in REST sites. In rivers, there were no visible differences in concentrations of Fe, phosphate, DOC, K, Mn or turbidity in treatment sites compared to controls following restoration (Figure 4.3).

POC, SPM and ANC showed seasonal increases in concentrations in summer 2013, 2014 and 2015, with REST sites showing the largest increases. As the magnitude of these was similar pre- and post-restoration, this suggested no clear effect of restoration and for POC and SPM the treatment*period interaction was not significant (X=6.26, p=0.1808 and X=0.38, p=0.9893, respectively). For ANC, in rivers the control sites were higher than the treatment in summer 2015 (post-restoration) but more similar at other times (Figure 4.3p).
We found a significant effect of restoration on Al concentrations, relative to the controls (X=10.09, p=0.0389). The effect of restoration on Al was less consistent across the stream classes, with large differences across FOR and REST sites (Figure 4.4). Only two out of the four restoration streams (DK2, DK5) showed increased concentrations following restoration, which occurred from July 2015 (Figure 4.4a,d). The other two restoration streams (DK6 and DK4) along with BOG, FOR sites and rivers exhibited considerable temporal variation but no clear seasonal pattern (Figure 4.4b,c).
The FOR and REST sites on the stream draining restoration block DK2 showed very similar temporal patterns of Al, both increasing in summer 2015 (Figure 4.4a). As the FOR site, was designed as a control, the source high Al may have been upstream of the restoration. Al concentrations in this DK2 stream were also higher than any other location in the study.

Figure 4.4: Time series of Al concentrations from May 2013 to December 2015, at individual stream and river sampling sites (a) DK2 stream control (FOR) + treatment (REST), (b) DK4 stream control (FOR) + treatment (REST) (c) DK6 stream control + treatment + downstream (all REST), (d) DK5 stream treatment (REST) (e) independent forest (FOR) and bog control streams (BOG) and (f) River Dyke sampling sites (BASE-R and REST-R) and (g) River Halladale sampling sites (BASE-R and REST-R). We have presented Al
concentration by site due to the large variation between sites and the varying response to restoration, which could not be adequately observed when plotted by class.

4.3.4 Pass rates for statutory WFD and drinking water standards

In both river classes (BASE-R and REST-R) across the whole study, there was a pass rate of $\geq 78\%$ when considering the Scottish Government WFD “high” quality standard limits for temperature, dissolved oxygen (DO), ANC, NH$_4^+$ and pH (Figure 4.5). These pass rates were not significantly affected by restoration (X, p values, Appendix 4.1). For NH$_4^+$, there was a 100% pass rate for the high quality status, while for pH ~90% of readings classified quality as “high”, with the remaining time being “good”, except on one occasion at REST-R sites post-felling. For ANC in both BASE-R and REST-R sites, a small number of samples achieved only “moderate” status post-restoration, while pre-restoration, samples were always either “high” or “good” quality. Two samples from the post-restoration period (REST-R sites) failed to reach even the “poor” threshold for ANC (hence the bar on Figure 4.5d) does not add up to 100%.

Post-restoration phosphate concentrations in BASE-R and REST-R sites only attained a “high” standard on 53 and 46% of occasions respectively (as opposed to 58 and 64% of occasions pre-restoration; Figure 4.5f). Pre-restoration, phosphate achieved “good” quality for the remainder of time (<9 $\mu$g P L$^{-1}$). Post-restoration in REST-R sites, there were fewer occasions when “good” criteria were met than at BASE-R sites. There were also more samples achieving just “moderate” status in REST-R sites and some (5% samples) where “poor” status was measured. There were no significant differences in pass rate at the “high” standard level as a result of forest-to-bog restoration between BASE-R and REST-R sites (X=0.90, p=0.3427).
Figure 4.5: Pass rates (%) for ecological and chemical standards for EU WFD applied to Scottish rivers for river baseline (BASE-R) and river restoration treatment (REST-R) sites pre- and post-restoration. To achieve “high” status for any variable the parameter must
exceed (e.g. > 5.1 pH) or fall below (e.g. < 20ºC) a threshold. Failing this “good”, “moderate” or “poor” status can be achieved. For pH, DO and ANC higher values indicate higher water quality. For temperature, NH₄⁺ and phosphate lower values indicate higher water quality. The WFD standards quote ammonia-N (NH₃), instead of ammonia-N (NH₄⁺), however here they are both equivalent measures.

Pass rates for bioavailable Cu, Mn and Ni were generally high in both river classes pre- and post-restoration, with Mn and Ni passing almost 100% of the time during the study against the Scottish Government WFD standards (Figure 4.6). The pass rate for Zn was ≤ 50%, in both BASE-R and REST-R sites, with no significant differences arising from restoration (X = 0.01, p = 0.9089). Despite the high pass rate for bioavailable Mn (limit = 123 µg L⁻¹) based on the Scottish Government WFD standards, the pass limit for the UK drinking water standard is 50 µg/L. As such, the pass rate against this criteria was slightly lower in both river classes, while BOG and REST sites had a pass rate of ≤ 56% for Mn in drinking water (Figure 4.7d).

Figure 4.6: Pass rate (%) for river baseline (BASE-R) sites and river restoration treatment (REST-R) sites, pre-restoration (pre) and post-restoration (post), for concentrations of bioavailable metals calculated with the M-bat UK Government tool (UK TAG, 2014b). To pass, concentrations must not exceed the bioavailable metal standards of: Cu - 1 µg L⁻¹, Mn - 123 µg L⁻¹, Ni - 4 µg L⁻¹, Zn - 10.9 µg L⁻¹
Generally, when considering drinking water standards, stream classes had a lower pass rate than river classes but none of the drinking water standard pass rates were significantly affected by forest-to-bog restoration (Appendix 4.1).

Al pass rates were higher ($\geq 96\%$) in rivers and BOG (stream) sites, while lower in FOR and REST sites (63-83\%), both of which saw a slight (11-14\%) decrease post-restoration (Figure 4.6a). The River Halladale had the lowest Al concentrations, which never exceeded the 0.2 mg L$^{-1}$ recommended drinking water limit (DWI, 2010), while the streams were often above this threshold. Post-restoration mean concentrations in both FOR and REST sites were close to the 0.2 mg L$^{-1}$ drinking water limit. In all classes drinking water pass rates were high for Cu and Ni ($\geq 77\%$ pass rate), with slight increases in the pass rates for Cu, post-restoration (Figure 4.6b,e).

Pass rates were most variable for Fe, with lowest pass rates in REST sites ($\leq 36\%$) and highest pass rates in BASE-R sites ($\geq 84\%$; Figure 4.6c). Finally, the lowest turbidity pass rates also were in REST sites ($\leq 67\%$), with the lower pass rate in the pre-restoration period (Figure 4.6f). For turbidity BOG sites changed the most between pre- and post-restoration (decreased 8\%).
Figure 4.7: Pass rate (%) for UK drinking water standards in each watercourse class (bog stream control sites (BOG), forest streams control sites (FOR), restoration treatment stream sites (REST), river baseline sites (BASE-R) and restoration treatment river sites (REST-R)) during the pre-restoration (solid bars) and post-restoration (hatched bars) periods. To pass, concentrations must not exceed the drinking water standards: Al - 200 µg L$^{-1}$, Cu - 2 µg L$^{-1}$, Fe - 1000 µg L$^{-1}$, Mn - 50 µg L$^{-1}$, Ni – 20 µg L$^{-1}$, Turbidity – 4 NTU.
4.4 Discussion

4.4.1 Effects of forest-to-bog restoration on water chemistry

In this study, changes in stream water chemistry observed following restoration fell broadly into two groups: 1) changes in soluble chemical species which are known to leach from brash and logging residues and 2) increased suspended particulates (e.g., turbidity) from physical disturbance and erosion.

The significant increases in concentrations of soluble chemical species observed in our study (phosphate, Al and Fe), have all been found by others following forest felling (Cummins and Farrell, 2003a; Finnegan et al., 2014b; Muller et al., 2015; Table 4.3). Increased stream water phosphate concentrations can be associated with historic phosphate fertiliser applications (Renou-Wilson and Farrell, 2007). However, in our study, phosphate fertiliser was applied in 2001 within the River Dyke catchment, but, not within any of the restoration areas studied here (Forestry Commission, 2016). Other studies of blanket peatland felling have also found increased phosphate in streams, without previous fertiliser application (Cummins and Farrell, 2003a). Therefore, the decomposition of tree biomass (brash and needles), was the likely mechanism for phosphorus release to watercourses (Chapter 3; Kaila et al., 2012; Asam et al., 2014), rather than an excess in soil from fertilisation. Although we found elevated mean phosphate concentrations (4.4 fold) in REST sites post-restoration, the larger range in individual stream concentrations (increasing from June 2015; up to 800 µg L\(^{-1}\)), was similar to that of other studies of peatland felling on stream water (Cummins and Farrell, 2003a; Rodgers et al., 2010; Finnegan et al., 2014b). These can persist for up to 4 years post felling (Rodgers et al., 2010; Table 4.3) and can continue to occur as seasonal peaks in the summer months (Cummins and Farrell, 2003a).

Similarly, increased stream water K and Mn (~2 fold) occurred in our study following restoration. These are both known to be affected in streams by conifer felling (Rosén et al., 1996; Cummins and Farrell, 2003b; Table 4.3), with Mn released from needles (Asam et al., 2014a) and K from brash decomposition (Fahey et al., 1991; Palviainen et al., 2004b). A greater effect size on K that what we observed here, has been found in other studies (~ 4 fold increase), which declined after two years (Cummins and Farrell, 2003b), while Muller and Tankéré-Muller (2012) found similar (~ 2 fold) increases in Mn increases occurring during the spring and summer, one-year post-felling on blanket peat.
Table 4.3: Summary of water quality changes following conifer felling in catchments with peat or organic soils from this study and other European studies. Effects are for various water quality parameters given as direction (↑ ↓), approximate mean magnitude (mag.) and longevity of effects (years). n.e. denotes no effects of felling / restoration.

<table>
<thead>
<tr>
<th>Study</th>
<th>Location</th>
<th>DOC</th>
<th>Phosphate</th>
<th>K</th>
<th>Mn</th>
<th>Fe</th>
<th>pH</th>
<th>SPM/POC</th>
<th>NH₄⁺</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>mag.</td>
<td>mag. years</td>
<td>mag. years</td>
<td>mag. years</td>
<td>mag. years</td>
<td>mag. years</td>
<td>mag. years</td>
<td>mag. years</td>
<td>mag. years</td>
</tr>
<tr>
<td>This study</td>
<td>Flow Country, UK</td>
<td>↑1.3</td>
<td>&gt;1</td>
<td>↑1.9</td>
<td>&gt;1</td>
<td>↑2.0</td>
<td>&gt;1</td>
<td>n.e.</td>
<td>n.e.</td>
<td>n.e.</td>
</tr>
<tr>
<td>Muller et al. 2015</td>
<td>Flow Country, UK</td>
<td>↑1.5</td>
<td>1</td>
<td>↑~2.0</td>
<td>1</td>
<td>↑~2.0</td>
<td>1</td>
<td>↑1.5</td>
<td>1</td>
<td>↑1.5</td>
</tr>
<tr>
<td>Cummins and Farrell, 2003a,b</td>
<td>West Ireland</td>
<td>↑&gt;1.5</td>
<td>2</td>
<td>↑&gt;10</td>
<td>2</td>
<td>↑1.2</td>
<td>2</td>
<td>↑2</td>
<td>↑1.2</td>
<td>2</td>
</tr>
<tr>
<td>Finnegan et al. 2014</td>
<td>West Ireland</td>
<td>↑2.0</td>
<td>&gt;1.5</td>
<td>↑2.0</td>
<td>&gt;1.5</td>
<td>↑2</td>
<td>5</td>
<td>↑2</td>
<td>↑1.5</td>
<td>2</td>
</tr>
<tr>
<td>Rodgers et al., 2010</td>
<td>West Ireland</td>
<td>↑&gt;1.5</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Rosen et al., 1996*</td>
<td>Central Sweden</td>
<td>↑1.9</td>
<td>8</td>
<td>↓</td>
<td>↓</td>
<td>↑2.5</td>
<td>8</td>
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<tr>
<td>Lofgren et al., 2009**</td>
<td>Northern Sweden</td>
<td>n.e.</td>
<td>2</td>
<td>↑2.0</td>
<td>2</td>
<td>n.e.</td>
<td>2</td>
<td>n.e.</td>
<td>n.e.</td>
<td>2</td>
</tr>
<tr>
<td>Nieminen, 2004</td>
<td>Southern Finland</td>
<td>↑&gt;1.5</td>
<td>4</td>
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mag. indicates approximate mean concentration change post-felling across the study period (years), ↑ denotes increasing concentrations and ↓ a decrease in values (only observed for pH). Most 1-2 year effects are found here due to maximum length of study - actual effects may last longer. * mainly mineral soils, ** only part of these stream catchments are peat.
Interestingly there were no increases in nitrogen (N) species post-restoration, which is commonly reported following conifer felling (Neal et al., 2004; Asam et al., 2014b; Palviainen et al., 2014). In other work, increased nitrate (NO$_3^-$) and NH$_4^+$ were found to last four years post felling (Nieminen, 2004), which suggests that effects on stream water N could potentially occur longer term, in future years. Increased concentrations of N compounds may first occur as there is a reduction in N uptake once trees are removed (Rosén et al., 1996), and then, as decomposition of brash and needles occurs (Hyvonen et al., 2000). However, from a decomposition perspective P is known to be released faster than N (Moore et al., 2011), which may explain why in the first year following restoration, we did not observe increases in N.

There were also visible increases in DOC (31 %) in REST sites following restoration (but statistically non-significant). Increased DOC has been widely noted following conifer harvesting (Table 4.3) and has been attributed to both brash decomposition (Hyvonen et al., 2000; Palviainen et al., 2004a) and a rising water table which caused enhanced decomposition in rewetted peat (Nieminen et al., 2015). DOC can be associated with Al and Fe by adsorption to DOC molecules (McKnight and Bencala, 1990; Krachler et al., 2010). In our study, both Fe and Al were found to increase following restoration streams, with maxima occurring in August 2015, along with peak DOC concentrations. However, increased Fe is more associated with groundwater and its influence on watercourses (rather than peatland felling); although it can associated with sediment inputs to watercourses (Björkvald et al., 2008) or be released by changing redox conditions within the peat and with seasonal water table movement (Muller et al., 2015) and. Therefore, the increasing water table in restoration sites (post-restoration; Chapter 3) may have contributed to increasing Fe stream concentrations.

In our study, we observed increased Al concentrations in two of the four restoration streams sampled (DK2 and DK5 streams, respectively), in the post-restoration period. However, in the DK2 stream the (FOR) control site exhibited an almost identical temporal pattern to the REST site in the post restoration period, also period showing increased concentrations (~3 fold) from summer 2015. This suggests increased Al was not an impact of restoration here i.e. not associated with felling (brash decomposition) or drain blocking and that there may be other site-specific factors influencing Al release.
The FOR control site on the DK2 stream, may have received high Al inputs from activities indirectly associated with restoration. The DK2 stream flowed alongside a gravel/ sand covered forest track. This track may have been disturbed upstream of the FOR control site, by movements of the harvesting machinery and released mineral material containing Al e.g. (Soulsby and Reynolds, 1993). Muller and Tankéré-Muller (2012) attributed increases in Al in water draining from felled sites to a long-term effect of disturbance of the underlying mineral layer during ploughing and planting. As some of the peat around the DK2 stream was shallow (~30 cm), the same mechanisms could partly explain elevated Al concentrations in both FOR and REST sites.

However, we can only conclude that restoration did not directly impact Al concentrations, but mechanical disturbances to access tracks may have caused some spatially localised concentration increases.

Increases in SPM, POC and turbidity were observed at REST sites both pre- and post-restoration in summer 2013, 2014 and 2015 and were of a similar magnitude in 2013 and 2015, which explains the high score on the PRC analysis for these variables. Pre-restoration, the concentration increases were associated with high flows occurring after summer droughts (low precipitation summer 2013; Appendix 5.3, 5.4). As there were no droughts occurring in summer 2015, compared to a very dry summer in 2013, this may link the 2015 concentration increases (from July – November 2015) with restoration. In response to peatland conifer harvesting in Ireland, increased SPM was found in the first six months post-harvest (spring/summer 2011) after which it declined, during a study lasting 15 months post-harvest (Finnegan et al., 2014b; Table 4.3). In this study, maximum concentrations of 481 mg L\(^{-1}\) SPM occurred during April storms, whereas in our study, maximum concentrations were only 100 mg L\(^{-1}\) (although storms were not specifically targeted in our study). The use of silt traps in addition to drain blocking in our restoration sites, may have successfully prevented a significant increase in SPM in streams and rivers affected by restoration. However, the effects of clear felling (harvesting profitable stems) on increased suspended solids have been known to last >10 years (Palviainen et al., 2014), therefore, declines observed in shorter-term studies (less than one year) may be temporary (and due to seasonal cycles).

Generally, the effects of forest-to-bog restoration were restricted to streams directly receiving drainage from restoration sites; Muller et al. (2015) also found that the effects of management were detectable within a small area and not in main outlet streams. This
may have been associated with the presence of un-felled buffer zones, which can act to nullify obvious changes in the chemistry of the main stream (Löfgren et al., 2009). In the present study, restoration streams (REST) flowed directly to main rivers (REST-R), but, streams were small in comparison to the rivers Dyke or Halladale. REST effects were thus easily diluted and rendered not detectable at river sites, even immediately downstream of the stream confluence. This was also found by Rodgers et al. (2010), where the main river was not impacted following peatland felling. In our study, the only differences in REST-R sites (post restoration) was a divergence in ANC concentrations between river baseline and treatment sites from August to October 2015. As there were no differences observed in ANC at stream sites, this suggests restoration was not the main driver at river sites. ANC was recommended as a key stream health indicator in a UK wide assessment of forestry impacts on water quality (it indicates the balance between weathering and acidification; Neal and Reynolds, 1998). Therefore, it seems positive from a water quality perspective that no significant change was observed following forest-to-bog restoration.

4.4.1 Implications for management - catchment area undergoing restoration

Felling a smaller proportion of a catchment is known to have fewer effects than felling a larger area (Nieminen, 2004), with one study from a mixture of peat and mineral soils suggesting 30% of the catchment as a threshold before significant effects are measured (Palviainen et al., 2014). In our study, the percentage of REST (stream) catchments felled ranged from 3% (DK4 stream), to 8% (DK2 stream), 9% (DK5 stream) and 23% (DK5 + DK6 stream, at sample point 10). These areas were estimated from the restoration area within the stream catchment including fractions of forestry blocks split by catchment boundaries. However, due to the altered hydrology present in forest blocks (i.e., from artificial drainage, collector drains and plough furrows), the actual area contributing to the stream catchment may well have been larger. Regardless of this, the calculated areas still provide a guide with which various levels of restoration impact can be associated.

It could be hypothesised that the largest post-restoration changes in water chemistry would occur where the largest percentage of catchment area was felled (DK5 + DK6 stream). However, of the impacted water chemistry variables, only K increased to concentrations that were higher (>2 fold) here, than in any other REST site. The same peak concentrations of phosphate and Mn also occurred in the DK2 and DK5 stream,
where smaller proportions of the stream catchment were felled. We suspect this may be due to the DK5+DK6 stream, having a larger unplanted area between the restoration sites and stream, which could have acted as a buffer zone in attenuating leaching of nutrients to the stream (Väänänen et al., 2008). Therefore, in our study, site-specific factors also are important in determining the impacts of restoration on stream chemistry.

4.4.1.2 Implications for management – felling methods

The methods of forest-to-bog restoration in this study comprised 'standard' or 'enhanced' felling, where standard felling harvested stems only, leaving brash on site and enhanced felling removed brash and stems, followed by roadside chipping of the brash. Mulching was also carried out on smaller trees, and only occurred in the DK4 stream catchment. The DK4 stream was the one where fewer concentration increases were observed compared with the other REST sites. However, since the DK4 site also had a smaller percentage of the catchment undergoing restoration we cannot speculate whether mulching has a greater or lesser impact than felling on stream chemistry. Elsewhere within the River Dyke catchment, the total area mulched was smaller areas than that felled (10-15% on average).

In the short term mulch may pose a risk to water quality (Moffat et al., 2006) as it could increase plant available soil nitrogen (Rhoades et al., 2012), which can be leached to streams (e.g. Asam et al., 2014b). However, there may be temporal trajectories over which mulch releases and accumulates nutrients. With conifer mulch (Pinon Pine and Lodgepole Pine) following the initial release of nitrogen, soil nitrogen availability was found to decrease after one year and then increased 3-5 years later (Rhoades et al., 2012). It is likely that elements release from brash decomposition will also be released from mulch in the initial decomposition stage, but a greater surface area in mulch than brash could enhance this effect (Hyvonen et al., 2000). On the other hand, mulch may be useful in preventing the leaching of sediment (Foltz and Wagenbrenner, 2010).

Brash removal (enhanced felling) may be an effective technique to reduce the effects of felling on streams by removing a major source of DOC and plant nutrients (Palviainen et al., 2004a, 2004b; Asam et al., 2014b). It has been found to be effective in reducing nutrient leaching to runoff in whole-tree harvest sites (O’Driscoll et al., 2014b), although another study found that it did not significantly reduce nutrient export (Kaila et al., 2015). At the stream and river sampling scale, where the catchments drained both standard and
enhanced fell areas, it was not possible to separate the effects of areas with and without brash removal. However, we have studied the effect of both separately on pore and surface water and found differing trajectories in water chemistry changes (Chapter 3).

Felling only small percentages of stream catchments at a time (≤ 23%), would be a good management strategy to minimise impacts to rivers, and limit those to streams. However, the total area undergoing restoration between October 2015 and December 2015, in the River Dyke catchment was 174 ha (3% of the catchment area). Thus there was a larger area with the potential to impact on the River Dyke, than that around the streams sampled in this study. Increasing concentrations of metals and nutrients following felling on blanket bogs have been found to last at least two-four years (Cummins and Farrell, 2003b; Rodgers et al., 2010). However, a recent study found that ‘standard’ felling (not harvesting brash) of forestry in Finland can increase the export of N, P and SPM from boreal (peat + mineral) catchments for many years (>10 years) after felling (Palviainen et al., 2014). Therefore, we can anticipate that with continued forest-to-bog restoration in the same stream catchments within two-four years, the total felled area will increase with both the new and current restoration areas contributing to water quality changes. This potentially may lead to greater concentration changes and greater impact on streams and the Rivers Dyke and Halladale.

4.4.1.3 Implications for management - drain blocking and silt traps

In looking to mitigate against water quality changes, the use of silt traps was an additional measure to drain blocking, to slow the flow of runoff water from the restoration plots to streams and rivers, and to retain sediment. Although there were some visible increases in SPM and turbidity post-restoration in REST (stream) sites, there were no significant differences in REST sites in the post restoration period relative to controls. This suggested that silt traps (installed in triplicate along with drain blocking) were effective in preventing the transport of sediment to streams and rivers, despite this being a common impact of harvesting on streams (Finnegan et al., 2014b; Palviainen et al., 2014). Out of the four REST streams monitored in this study, the DK2 stream was blocked as a drain, due to being channelled into forest drainage before entering the River Dyke. None of the other streams were blocked in this way; instead collector drains for restoration areas were blocked before entering the streams, with a series of plastic piling dams and silt traps. Drain blocking may have helped raise the water table level and thus contributed to
changes in water chemistry associated with decomposition within the peat matrix. This would have included DOC production along with Fe (Fenner et al., 2001; Nieminen et al., 2015).

4.4.2 Water chemistry - general temporal trends and drivers
Temporal patterns in water chemistry were significant in our study. Fourteen percent of the variation in water chemistry was explained by the interaction of time and the class (treatment), similar to what was observed for peatland surface water in a study of restored bogs in Canada (Andersen et al., 2010).

The effect of restoration on “biologically driven” water chemistry variables (i.e., DOC and phosphate) was most obvious in summer and autumn months. This fitted the natural seasonal cycling observed in pre-restoration years where higher summer concentrations were seen, as also noted in several Irish peatland studies (Cummins and Farrell, 2003b; Ryder et al., 2014). As these variables are associated with the annual cycle of growth and decay, the annual temperature cycle is known to be a major driver (Muller et al., 2015) in enhancing decomposition during warmer months (Bonnett et al., 2006). Therefore, this seasonal pattern was found for most parameters affected by restoration (significant and non-significant increases), including metals associated with brash and needle decomposition (K and Mn; (Kaila et al., 2012; Asam et al., 2014a) and with water table changes and the redox conditions (Fe; Küsel et al., 2008). On the other hand, variables associated with physical disturbance (turbidity and SPM) were strongly affected by dry periods (build-up of sediment available for release) and flushing during subsequent periods of high flow (Rodgers et al., 2011; Finnegan et al., 2014b).

4.4.2.1 Implications of seasonality for management
The strong seasonal cycle, within which increasing concentrations were found (post-restoration), suggests that the timing of management may have a weaker influence on the timing of potential impacts in watercourses and that concentration increases may be tied with underlying seasonal trends, as found by Cummins and Farrell (2003a). There are currently no general restrictions on seasonal felling (Forestry Commission, 2011). Felling occurring in the summer thus may result in an immediate (and potentially more harmful) increase in concentrations.
Another important seasonal consideration for forest-to-bog restoration in the Dyke and Halladale catchments is Atlantic Salmon spawning, which occurs in October or November (Soulsby et al., 2001; Hendry and Cragg-Hine, 2003), in the Rivers Dyke and Halladale. In our study, felling commenced during the spawning period, due to a delay to the planned commencement (until October 2014). During egg incubation, hatching and the earliest developmental stage (alevins), salmon are sensitive to sediment (egg smothering), pH, Al and DO (Mills, 1989; Buckler et al., 1995; Malcolm et al., 2003). However, increased monitoring every two weeks from October to December, showed no changes in river water quality during this initial period which was critical for Salmonids. This may have been (at least partly) due to the use of sediment traps in addition to collector drain blocking, and, because of felling on small proportions of the REST catchments at any one time (3-23 %).

4.4.3 Potential impacts of restoration on statutory water quality standards and salmonid habitat

The most important water quality parameters in the study, considered nationally and internationally to pose an ecological or human health risk, are those in WFD or drinking water standards (European Commission, 2000; DWI, 2010). The only parameters included in these standards for which we observed significant concentration increases following restoration were phosphate and Fe (in restoration streams). Although we do not attribute increased Al concentrations to a restoration effect, the associated impacts of forestry/access track disturbances suggest Al should be included in the discussion of water quality standards. Together these parameters (phosphate, Fe and Al) could be considered as the most ecologically significant impacts in this chapter.

In terms of the WFD standards, these solely apply to rivers; therefore, the pass rate regarding the “high” WFD criteria for phosphate was only assessed in river classes where there were no significant changes in pass rates or concentrations. A “good” status within the WFD represents a system where there is minimal anthropogenic impact (European Commission, 2016b). This was achieved during 75% of the post-restoration period for phosphate in REST-R sites (but 100% of the pre-restoration period). The period when a “good” status was not achieved (i.e., 25% of the post-restoration period) was during the summer of 2015.
For phosphate, the main risk is through eutrophication and the promotion of algal blooms which can reduce light penetration and (upon decay) consume oxygen (Smith et al., 1999; Painting et al., 2007). This is more of a concern in static water bodies or in coastal marine waters where high concentrations of both nitrate and phosphorus can be delivered (Painting et al., 2007), e.g., into Melvich Bay in the case of the river Halladale. However, concentrations of nitrate were lowest in the summer (data not shown) when phosphate was higher (which may help prevent negative impacts).

For Al, the drinking water standard was passed 100% of time in REST-R sites, pre- and post- restoration (and slightly less than 100% was observed in BASE-R sites). In REST (stream) sites, there was a lower pass rate post-restoration but this was not significantly different to that of the pre-restoration period. However, in our study, only the River Halladale may be used (to a limited extent) for drinking water and here Al concentrations were always less than 0.2 mg L\(^{-1}\) (drinking water limit) during this study, suggesting a low risk level for Al. Similarly, for Fe, there were no significant effects of restoration on the pass rate for streams or rivers, the latter having pass rates \(\geq 77\%\), and there would be low risk to human health from these river Fe concentrations regardless (WHO, 2003).

Aside from human health, Atlantic Salmon, which use the streams and rivers in the catchment for spawning, are also sensitive to changes in water chemistry. In particular, free Al\(^{3+}\) ions, termed inorganic monomeric Al, can impair early development (and smoltification) by particularly affecting gill functioning (Kroglund et al., 1999) at low (25 µg L\(^{-1}\)) concentrations (Kroglund et al., 2008). This form of Al is present in waters of low pH, e.g., at pH 4 almost 100% of the Al present will be in this form whereas at pH 6 this drops to almost 0% (Dobbs et al., 1990). It is possible to measure Al\(^{3+}\) directly using complex extraction methods but it wasn’t specifically measured in this study. Several studies have also estimated Al\(^{3+}\) by using Al speciation prediction models e.g. ALCHEMI (Schecher and Driscoll, 1988) and WHAM model (Tipping, 1994). However, these commercial models require additional data (Total-Al, F; Schecher and Driscoll, 1987; Cory et al., 2007) which were not collected as part of this study. A UK Environment Agency review proposed that Al\(^{3+}\) could be predicted, so that measures of total dissolved aluminium could be used to predict toxic and available species which are more environmentally relevant (Environment Agency, 2007). However, they concluded that there was currently no accessible way to do this and that evidence was too broad ranging to even come up with environmental quality standards for threshold Al\(^{3+}\) concentrations.
(Environment Agency, 2007). This is partly due to a range of studies which have found lethal or sub-lethal effects on salmon from a wide range of pH and Al$^{3+}$ combinations (Kroglund et al., 2008). In the future, direct measurements or reliable prediction of Al$^{3+}$ concentrations at a range of pH could help build a “risk curve” to identify thresholds of water quality for Salmonids following changes in land-use.

4.4.3.1 Targeted mitigation for Aluminium and phosphate

To minimise Al and phosphate inputs to rivers (owing to potential toxicity to Atlantic Salmon and eutrophication respectively), there are potential additional management interventions to prevent concentration increases, or remove high concentrations from streams. One method could be to use sorbents (to bind Al) which remove Al from streams. However, Al oxide is used in water treatment as a sorbent for removal of heavy metals (Hua et al., 2012) and DOC (Chow et al., 2009), therefore many studies focus on using Al as a sorbent rather than removing it. Recent work has shown the potential of aquatic plants to remove Al, where *Camboda piauhyensis* removed 87\% of dissolved Al through bioaccumulation (in a 0.2 mg L$^{-1}$ Al solution; Bakar et al., 2013). Although *C. Piauhyensis* is completely unsuitable to use (non-native aquarium plant), it suggests there may be potential in the use of native aquatic plants to remove Al. Other novel methods of Al removal include the use of activated carbon (removed 60\% of Al at concentrations of 5 mg L$^{-1}$; Pour et al., 2014) and beach cast seaweed (removed 50\% of Al at 100 mg L$^{-1}$; Lodeiro et al., 2010). However, they may not be as effective at lower Al concentrations observed in our study (< 1 mg L$^{-1}$) and neither are easily implemented solutions. One concern of longer-term use of seaweed as an Al sorbent is that seaweed decomposition could release nutrients into the streams (Nędzarek and Rakusa-Susczewski, 2004), even in a situation with water diversion or extraction, thus exacerbating already high concentrations of phosphate, so it is not a practical solution for forest-to-bog restoration.

Phosphate removal from water is commonly implemented in wastewater treatment e.g. in activated sludge treatment where phosphate is removed by bacteria (Fuhs and Chen, 1975). In simpler systems, phosphate can be removed from solution by electrocoagulation with Fe or Al electrodes (Irdemez et al., 2006), though this requires electricity. A more passive system is to use red mud (a waste product of aluminium oxide production) which can adsorb phosphate through the high percentage of Fe (Huang et al., 2008). However, as this material contains Fe and Al oxides, in a flow-through stream system it may leach
these to stream water. Therefore, a solution to removing both Al and phosphate is difficult as potential materials which remove one may leach the other into streams. Instead of trying to remove them from the streams, it may be more efficient to prevent them entering the streams in the first place. In general, we recommend felling small percentages of catchments (<23 %), removing brash and needles, and the use of sediment traps in addition to collector drain blocking, although minimising disturbance to access tracks and to the surface of shallow peats may prevent the mobilisation of mineral material and help reduce Al leaching.

It has been shown that established riparian buffer areas (birch, oak and rowan; 5 years old) can be effective in retaining phosphate following felling (Finnegan et al., 2012). However, these “traditional” buffers of 15-20 m of deciduous trees between the felled area and the stream may not be efficient in immobilising phosphate release during storm events (Rodgers et al., 2010). They also may not align with the objective of forest-to-bog restoration, to regenerate of open bog habitat as the natural long-term state (Tallis, 1998; Tipping, 2008).

One study in Ireland, investigated the ability of 10 native grasses in to germinate rapidly in blanket peat forests and the effectiveness of these grasses in accumulating P (O’Driscoll et al., 2011). These results found that Holcus lanatus and Agrostis capillaris were most successful and since then several studies have sown these grasses in novel buffer zones, to mitigate the effects of felling on nutrients and SPM in streams (Asam et al., 2012b; O’Driscoll et al., 2014a, 2014b). One study found diverting runoff water from upstream felled areas, through a buffer zone using H. lanatus and A. capillaris reduced SPM and phosphate in runoff by 18% and 33% respectively (O’Driscoll et al., 2014a). Another proposed the use of “mini” buffers to retain phosphorus in felled areas, where contoured strips of peatland were seeded with H. lanatus and A. capillaris to utilise and retain phosphate (Asam et al., 2012b). This study found that the grasses established within two months and suggested they may be able to retain phosphate during high flow events (Asam et al., 2012b). Therefore, the strategy of many small buffers dealing with smaller water volumes may be more effective than one large buffer which has limited P retention capabilities (Rodgers et al., 2010).

This suggests there could be potential for seeded buffer areas in forest-to-bog restoration sites, to reduce leaching of nutrients and sediments to streams. However, in our study site, which is managed for nature conservation H. lanatus and A. capillaris are not suitable, as
it may not be appropriate to widely introduce them close to Natura 2000 designated blanket bogs. Alternative native grass species could be *Mollinia caerulea* and *Deschampsia flexuosa*, although *M. caerulea* was found to not germinate effectively on trial buffer plots (O’Driscoll et al., 2011). This was also true for *Eriophorum vaginatum* and *Juncus effusus* (O’Driscoll et al., 2011), therefore, native grasses to the Flow Country blanket bogs may be less effective in forming effective buffer zones.

Along with removing brash as a primary phosphate source (Palviainen et al., 2004a), the establishment of seeded buffers has been found to be more effective in removing P in runoff than either separately (O’Driscoll et al., 2014b). Thus, if a suitable species was found for use in forest-to-bog restoration sites, this may be an effective strategy in mitigating water quality changes, particularly as restoration continues and larger percentages of catchment areas may be felled. However, the monetary cost of such measures would need to be considered along with the benefits of a reduction in phosphate leaching to streams and rivers.

### 4.5 Conclusions

Forest-to-bog restoration resulted in increased phosphate (4.4 fold) and Fe (1.5 fold) in restoration streams but not rivers. Increased Al concentrations in some restoration and afforested control streams (1.5 fold) were associated with forestry/ access track disturbances. All of these appeared as an enhanced seasonal cycle, peaking in summer months. None of the pass rates for Scottish Government WFD “high” ecological status or bioavailable metals or UK drinking water standards were significantly affected by restoration. However, there were a greater number of occasions post-restoration (25%), when phosphate did not reach the target “good” status in rivers.

We attribute these limited effects to felling small percentages of catchment areas (3-23%) and the use of drain blocking and silt traps. For future restoration, we recommend following these measures. We further suggest the harvesting of brash and needles, to reduce leaching of phosphate although we were not able to test this here. With continued forest-to-bog restoration in the same stream catchments within two-four years, the total felled area will increase with both the new and current restoration areas contributing to water quality changes. Therefore, a potential solution to mitigate against water quality
deterioration may be to combine brash removal with the use of buffer areas, to reduce leaching of nutrients and SPM.
5. Aquatic Carbon export in the first year following forest-to-bog restoration

5.1 Introduction

The riverine transport of dissolved organic carbon (DOC) from land to ocean is a major element within the global carbon cycle (0.8 Gt C yr\(^{-1}\) exported; IPCC, 2007). Peatland catchments are a particularly important contributor to this export route due to their significance as terrestrial carbon stores (Hope et al., 1994, 1997b). Indeed, Scottish blanket peat catchments, which cover 23% of Scotland’s land area, are estimated to generate 53% of the DOC exported from British rivers. The Rivers Halladale and Thurso in Sutherland and Caithness export the highest mass of organic carbon of all UK rivers (Hope et al., 1997b).

Loss of carbon through riverine transport, termed aquatic carbon export, is a central part of the peatland carbon budget. It is particularly critical for peatlands which are a small sink in terms of the net ecosystem exchange (NEE) of gaseous carbon, as aquatic carbon export can then tip the overall balance to a net carbon source (Armstrong et al., 2010; Worrall et al., 2011), as observed, in a drained English bog by Rowson et al., (2010). In contrast, in an ombrotrophic peatland in southern Scotland, which was a larger sink for gaseous carbon but exported less aquatic carbon (one quarter of the NEE), the peatland remained a net carbon sink (Dinsmore et al., 2010).

DOC is the single most important component of the total mass of aquatic carbon within peatland systems (Dawson et al., 2002, 2004; Billett et al., 2010). Aquatic carbon is also found in other forms - as dissolved inorganic carbon (DIC), particulate organic carbon (POC) and dissolved CO\(_2\) and CH\(_4\), but all in much smaller proportions (Dinsmore et al., 2010, 2013; Figure 5.1). In turn, aquatic carbon export largely depends on the concentration of DOC in peatland porewater, which is controlled by decomposition rates within the peat, and on the transfer rate of DOC into the stream/river network (Billett et al., 2004; Dawson et al., 2004; Fenner et al., 2011). The total mass of carbon lost through the aquatic route is also, therefore, a function of the volume of water flowing out of the catchment (Littlewood, 1992).
Figure 5.1: Components of downstream aquatic carbon export. Size of boxes indicates relative proportions of each species to the total aquatic carbon pool in a UK peatland catchment. Typical literature ranges for each species are shown. Red borders represent species presented in this study. References are: [1] Dawson et al., 2002; [2] Dawson et al., 2004; [3] Dinsmore et al., 2013.

5.1.1 High flow storm events, seasonal and longer term effects on carbon export

It is important to account for high flow events (storms) when measuring aquatic carbon export as these result in much greater aquatic carbon export when compared to regular base flow (low flow) conditions (Hinton et al., 1997; Grayson and Holden, 2012). In UK blanket peatland catchments, around half of the total DOC exported is exported during high flows events, even though these events represent 10% or less of all stream flow conditions (Grieve, 1984; Clark et al., 2007). Thus they are considered to export a disproportionately high mass of carbon (Vinjili, 2012). This is replicated globally, although in continental and arctic climates, snow melt driven high flow events are the most significant for DOC export (Hinton et al., 1997).

During storms, absolute DOC concentrations have been found to either increase (Grieve, 1984) or decrease (Clark et al., 2008), but overall exported mass tends to increase with increasing stream discharge volume (Clark et al., 2007). It is thought that a decrease in DOC concentrations during storm events can occur in peatland catchments as base flow is through organic soil layers and rainfall causes further dilution in surface runoff (lower
in DOC; Clark et al., 2008). However, this is dependent on season (Eimers et al., 2008) and on conditions prior to the storm event (Grand-Clement et al., 2014). For example, during summer storms, stream DOC concentrations can increase if recently synthesised DOC is flushed out of the catchment by precipitation (Koehler et al., 2009). Higher DOC outputs have also been linked to increased temperature (Ritson et al., 2014) and higher summer biological productivity (Cummins and Farrell, 2003b). There are also longer term trends (over decadal timescales) which may be linked with trends in atmospheric pollutant deposition (Clark et al., 2010) and long term climate patterns. For example, in UK rivers between 1988 and 2000, a general increase in aquatic carbon export of 65% was observed, which appeared to be linked to rising temperatures (Freeman et al., 2001a).

5.1.2 Effects of peatland restoration on aquatic carbon exports

In addition to climate, land management practices can also have a significant effect on aquatic carbon export, due to changes made to local hydrology and associated impacts on decomposition within surface peat layers. For instance, following felling of planted conifers on blanket peatland, increased DOC concentrations were found in surface waters that were impacted by decomposing conifer foliage and litter, and additionally, increased stream DOC concentrations and fluxes were observed in the two years after felling (Cummins and Farrell, 2003b; Muller and Tankéré-Muller, 2012).

In a national study of peatland drain blocking across the UK, a trend towards reduced DOC concentrations in drainage water was found after blocking (Armstrong et al., 2010). There is also strong evidence that peatland restoration on open bog sites across the UK tends to be followed by a reduction in aquatic carbon export (Gibson et al., 2009; Wilson et al., 2011a), although this finding is not consistent across all sites (Armstrong et al., 2010). Differences between studies may well be influenced by certain site-specific factors, such as slope, which is an important consideration when positioning drain blocks (Holden et al., 2006). Slope influences water table depth (WTD), recovery and runoff production (Holden and Burt, 2003b), and therefore, DOC production and export during re-wetting.
5.1.3 The need to understand the effects of forest-to-bog restoration

Most evidence regarding changes in aquatic carbon export and steam water DOC concentrations following drain blocking relate to restoration on open bog sites (Gibson et al., 2009; Wilson et al., 2011a), formerly drained for agricultural reasons. The impacts of forest-to-bog restoration on water quality and aquatic carbon export, where a combination of tree removal and drain blocking are used, is largely unknown (Anderson, 2010; Muller and Tankéré-Muller, 2012). Altered biogeochemical cycles in pore water as a result of rewetting and brash decomposition may change stream DOC concentrations (Palviainen et al., 2004a; Muller et al., 2015), and hydrological changes due to reduced evapotranspiration (caused by tree removal) may affect the catchment water balance. For instance, increased stream flows have been observed following felling (Ahtiainen and Huttunen, 1999; Löfgren et al., 2009). The combination of increased DOC concentrations and increased stream flows may have significant effects on aquatic carbon export. An additional challenge in studies over a number of years is presented by the potential interaction of climatic variation (e.g. inter-annual variability in rainfall) with land management effects.

Current recommended targets for UK peatland restoration of 1 million hectares by 2020 (Bain et al., 2011) include a significant amount of restoration of afforested sites on deep peat which are no longer considered suitable for long-term forestry (Forestry Commission Scotland, 2015). This will result in many afforested peatland sites undergoing restoration over the foreseeable future, rather than continued management as forestry. This change in government policy has been driven by compelling evidence of the impact of plantation forestry on waders (Wilson et al., 2014), but also by the potential reduced losses of soil carbon (Morison et al., 2010; Chapman et al., 2013). It is now thought that protecting current soil carbon stocks and allowing potential recovery of carbon sequestration (by bog vegetation) is a more effective means of contributing to UK carbon targets than growing trees and allowing the surface peat to degrade (Hargreaves et al., 2003; Forestry Commission Scotland, 2015; Renou-Wilson and Byrne, 2015). Such policy change will thus contribute to the potential for 9 t CO$_2$e ha$^{-1}$ yr$^{-1}$ of abatement benefit from peatland restoration across the UK (Artz et al., 2012). However, the evidence base used to derive the above estimates is far from complete. Forest-to-bog restoration methods involve the use of specialist harvesting and mulching machinery, along with mechanical and manual damming of collector drains and forestry furrows. As such, the management practice itself
represents a significant disturbance to the peat surface. The short term effects (0-1 year) of this on the loss of aquatic carbon, immediately following restoration may be large (albeit short-lived), and need to be taken into account when considering potential carbon savings from restoration in comparison with continued forestry.

Therefore, the aim of this chapter was to determine the immediate effect of forest-to-bog restoration on the export of aquatic carbon, by comparing an open bog catchment, an afforested catchment and a catchment undergoing forest-to-bog restoration. This was achieved by measuring aquatic carbon export from outlet streams before and after management changes were implemented from autumn 2014. Additionally, we assessed the effects of seasonality and storm events on aquatic carbon export as well as the potential implications of these effects for management.

It is hypothesised that in the short term, the export of aquatic carbon will increase in the catchment undergoing restoration when compared to that of the open bog or afforested catchment. Firstly, due to additional DOC production and the flushing of this DOC from pore water as the water table rises following drain blocking. Secondly, in response to increased stream discharge as felling the trees will reduce interception in the catchment. It is further hypothesised that there will be seasonal variation in DOC concentrations and export, with the highest export occurring when DOC concentrations and discharge are highest. Therefore, storms events will also be seasonally important.
5.2. Methodology

5.2.1 Site description

This study was conducted on three blanket bog catchments around the RSPB Forsinard Flows National Nature Reserve in Sutherland (Figure 5.2). The first catchment held a mix of 197 ha of open bog and 215 ha of non-native forestry planted in 1982 and 1988 as a mixture of Sitka spruce and Lodgepole pine (which was located in the upper part of the catchment). Of this forestry, 49.7 ha were felled to commence forest-to-bog restoration from November 2014 to June 2015, which was 12% of the total catchment area. This was two of the seven restoration sites described in Chapter 2.2. Felling was carried out using a mixture of standard (stem only harvest) and enhanced felling (stem and brash harvest; Chapter 2.2). Stem and brash (tree tops and branches) harvesting was not completed until August 2015, which along with felling was considered as part of the post-management period. Collector drains in each of the restored sites were blocked in December 2013. Drain blocking was achieved with a sequence of three plastic piling dams, set at points where drains flowed out of each forestry block or reached adjoining watercourses. Additional sediment traps (using Hytex® geotextiles) were also installed. The lower section of the restoration catchment comprised of open bog with a small section (1.6 ha) of young broad leaved trees planted near the catchment outlet into the River Halladale.

The second catchment (afforested catchment in Figure 5.2) comprised of open bog (with bog pools) in the upper catchment and stream source area (159ha; ~40%) with the remainder of the catchment afforested (235 ha; ~60%) with non-native conifers (as in the restoration catchment). This was situated adjacent to the Dyke forest and the catchment outlet entered the River Halladale. The third catchment was 100% open bog and was approximately 5km south of the other two, with the stream flowing into the River Dyke.
Figure 5.2: Location of hydrological catchments used in this study. Blue – restoration catchment (yellow areas indicate the 49.7 ha which underwent forest-to-bog restoration management from Nov 2014 – June 2015). This catchment comprised ~50% forest and ~50% bog.
% open bog. Green – afforested control catchment, orange – open bog control catchment. ♦ represents stream sampling points.

All three catchments were underlain by migmatite rocks, comprising of psammite, pelite and semipelite, with some areas of glacial deposits and peat as the surface soil type (British Geological Survey, 2016). Peat depths vary from <1m to >7m in places. The open bog catchment contained a mixture of *Sphagnum* species, cotton grass and cross leaf heath which are typical species of a blanket bog (Forrest and Smith, 1975; Lindsay et al., 1988). Open bog plots surveyed in the vicinity had *Sphagnum* as the dominant species (38% cover) at randomly selected dipwell sites. Similarly, surveys showed ground vegetation cover in the restoration areas of the restoration catchment contained <3 % *Sphagnum* cover and were dominated by *Acrocarpus* mosses (49%) and vascular plants (42% cover). Ground vegetation was not surveyed in the afforested catchment, although nearby afforested plots were found to have mainly *Acrocarpus* mosses (49%) and 11% *Sphagnum* cover. Further catchment details are described in Table 5.1.

### 5.2.2 Stream discharge measurements

In each catchment, the outlet stream was instrumented with a stilling well holding a pressure transducer and thermocouple to continuously monitor stream depth and temperature at 30 minute intervals (Appendix 5.1). Stream depth and temperature were measured for 11 months prior to restoration and then for 14 months after the start of restoration activity (i.e. total of 25 months; November 2013 – December 2015 inclusive). Discharge was measured near to the depth logger in each stream under a range of flow conditions to allow construction of rating curves between discharge and depth (Figure 5.3; Shaw, 1994; Clark et al., 2007). These allowed the use of depth data to predict discharge and therefore estimate discharge for each stream at 30 minute intervals.
Table 5.1: Catchment descriptors

<table>
<thead>
<tr>
<th>Catchment</th>
<th>Restoration management (12% area – 49.7 ha)</th>
<th>Afforested</th>
<th>Open bog</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Area</td>
<td>412 ha</td>
<td>394 ha</td>
<td>74 ha</td>
</tr>
<tr>
<td>Bedrock</td>
<td>Mainly passamite with semipelite. Small areas of pelite with semipelite</td>
<td>Mainly passamite with semipelite. Small areas of pelite with semipelite</td>
<td>Pelite with semipelite</td>
</tr>
<tr>
<td>Soil Parent Material</td>
<td>Peat + small areas of hummocky glacial deposits: sand, gravel and boulders</td>
<td>Peat + small areas of hummocky glacial deposits: sand, gravel and boulders</td>
<td>Peat</td>
</tr>
<tr>
<td>Land cover</td>
<td>40% of catchment afforested (165.3 ha) – upper catchment 12% undergoing restoration (49.7 ha); 48% open bog (197 ha) – lower catchment.</td>
<td>60% afforested (235 ha), 40% open bog (159 ha) – upper catchment, stream source</td>
<td>100 % open bog</td>
</tr>
<tr>
<td>Management</td>
<td>Restored 49.7 ha; 20.5 ha from Nov 2014 and 29.2 ha from Mar 2015. Standard and enhanced felling. Felling complete end June 2015, harvesting complete beginning August 2015</td>
<td>N/A (Standing forestry)</td>
<td>N/A</td>
</tr>
<tr>
<td>Steam sampling location</td>
<td>NC 89373 51248</td>
<td>NC 90309 46769</td>
<td>NC 84846 44565</td>
</tr>
</tbody>
</table>
Figure 5.3: Discharge and stream depth relationships for sampling sites on (a) the restoration catchment (b) the afforested catchment and (c) the open bog catchment. These rating curves were used to estimate discharge in each stream at 30 minute intervals.

Discharge measurements were made using an impeller flow meter (Geoparks) using the velocity area method (Shaw, 1994) at approximately 20 cm intervals through a cross section of the stream for one minute. The velocity area method was unsuitable for very low (when impeller would not turn) or high flow conditions (unsafe to stand in stream). Therefore, an additional method of discharge measurement (flow dilution gauging) was used, where a known quantity of salt was added to the stream (Okunishi et al., 1992). By measuring the change in salt concentration over time at a fixed sampling point, discharge was determined. The discharge measures made using both methods (Appendix 5.1) were combined in construction of the rating curve for each outlet stream (Figure 5.3). The rating curve was produced using linear regression of (log transformed) discharge values on log transformed depth, which gave the best model fit. This was confirmed by checks of normality and homoscedasticity of residuals and that no strongly influential observations were present (Crawley, 2007). Hourly precipitation was measured using a
tipping bucket rain gauge (Davis Vantage Pro2Plus, Davis Instruments) connected to a logger that was located within the bog catchment (Figure 5.2).

5.2.3 Stream water sampling and aquatic carbon measurement
Stream water samples were collected at the main stream outlet of each catchment, during base flow and stormflow for DOC and DIC analysis from November 2013 to December 2015. Monthly samples were collected as part of the stream water quality sampling (Chapter 4.2.2), along with storm event sampling (section 5.2.4) and additional individual samples collected on an ad-hoc basis, giving a total of 264-394 samples per catchment. This sampling strategy increased the number of aquatic carbon measurements and improved coverage across all seasons which in turn enhanced estimates of DOC export. Sampling in the bog catchment began in April 2014, due to a change in choice of the control catchment (Appendix 5.1).

Sample preparation and analysis for DOC and DIC was carried out as described in Chapter 2.5, with the exception of samples from high flow events. In this case, sample collection was sometimes not possible until several days after the end of storm sampling, which delayed filtering and subsequent analysis. POC was measured only, on a monthly basis as part of the wider water quality analysis (Chapter 4.2.3).

5.2.4 Storm event sampling
Storm events (a precipitation event causing a defined rise in stream discharge; Grand-Clement et al., 2014) were specifically targeted using automatic water samplers (Hach Lange, Buhler 2000). Despite much research targeting storm events and high flows, because of their importance to calculating export (Clark et al., 2007; Armstrong et al., 2010; Wilson et al., 2011b), there is no standard definition or technique for sampling them (Grand-Clement et al., 2014), with many authors choosing an arbitrary rise in stream depth as an indicator. In this study, storm events were considered to be those that generated a minimum rise in stage height of 10 cm in the restoration catchment stream. Due to differing catchment characteristics and responses to precipitation, this rise was generally smaller in afforested and open bog catchments.

Storm events were sampled from January 2014 to November 2015, within all seasons and during both pre- and post-restoration management periods. A range of large and small
storm events were sampled with rises in stream depth from 10 to 69 cm in the restoration catchment. A summary of all storm events sampled is given in Appendix 5.2. Auto-samplers were set manually at or prior to the beginning of the storm, based on weather forecasts and discharge conditions in the River Halladale (using SEPA flow levels). Auto-samplers were set to sample at one or two hour intervals depending on how long the storm event was expected to last (to give either 24 or 48 hours of sampling). There were 20 occasions when automatic water samplers were set out. Of these, three were not classified as storm events as the rise in stage height was <10 cm in the restoration catchment stream. Therefore, a total of 17 storm events were sampled; eight prior to restoration management, seven during and two after restoration management (Appendix 5.2). However, in this study, all sampling from November 2014 (the beginning of restoration) was considered post-restoration. Before May 2014, only the afforested and restoration catchments were sampled during high flow events. From then onwards, all three catchments were sampled simultaneously. However, there were instances where one or more auto-sampler did not function for the entire duration of the storm, therefore, the number of samples collected from each catchment differed due to “missing at random” samples.

5.2.5 Calculation of carbon export
Carbon export was calculated using “method 5” of Walling and Webb (1985), which is based on the mean discharge and the mean discharge weighted concentration. This method of calculating aquatic carbon export is widely used (e.g. Clark et al., 2007; Dinsmore et al., 2013). Firstly, the load (kg carbon per unit time) was calculated as follows:

\[
Load = K \times Q_r \times \frac{\sum_{i=1}^{n} [C_i \times Q_i]}{\sum_{i=1}^{n} Q_i}
\]

where \( K \) is a unitless conversion factor for the time period of the calculation, \( Q_r \) is mean discharge from a continuous record in L s\(^{-1}\), \( Q_i \) is instantaneous discharge L s\(^{-1}\) and \( C_i \) is the instantaneous carbon concentration of the stream in mg L\(^{-1}\), for \( n \) number of samples. Equation 5.1 allows calculation of the mean carbon load per unit time which is then converted to an export flux in kg carbon per unit area, per unit time, by dividing the load by catchment area. The standard error (SE) of the load (and flux) estimate is calculated as follows:
\[ SE = F \times \text{var}(C_F) \quad [\text{Equation 5.2}] \]

where \( F \) is total discharge over the time period of the calculation and \( \text{var}(C_F) \) is the variance of the flow weighted mean concentration, which is calculated using the following equation:

\[
\text{var}(C_F) = \left[ \sum \left( (C_i \times C_F)^2 \times \frac{Q_i}{Q_n} \right) \right] \times \frac{\sum Q_i^2}{Q_n^2} \quad [\text{Equation 5.3}]
\]

where \( Q_n \) is the sum of all the individual \( Q_i \) values in the calculation (Hope et al., 1997a; Dinsmore et al., 2010) and \( C_F \) the flow weighted mean concentration (FWMC) is calculated as follows:

\[
FWMC = \frac{\sum C_i \times t_i \times Q_i}{\sum t_i \times Q_i} \quad [\text{Equation 5.4}]
\]

Where \( t_i \) is the time step between subsequent concentration measurements. Flow weighted mean concentrations were calculated to indicate seasonal averages which were not biased due to periods of very high or very low flows, to allow inter-seasonal comparisons. When there was more variation in the carbon concentration in the stream, the error around the load and flux estimate was greater, as this formula pays greater attention to variation in instantaneous concentration rather than flow (Hope et al., 1997a). Carbon export was calculated on a monthly, seasonal (3 months) and annual basis for DOC and DIC. For POC, only seasonal and annual exports were calculated, as only one sample per month was collected. Therefore, total aquatic carbon export was also calculated on these temporal scales.

Storm samples were included in all seasons from January 2014. Seasons were defined using the hydrological year; 1st October-30th September, split into four seasons to allow fitting within the calendar year (Gordon, 2004; Dinsmore et al., 2013). Seasons were defined as autumn (October, November, December), winter (January, February, March), spring (April, May, June) and summer (July, August, September).

The use of the Walling and Webb method of calculating export is widespread (Dinsmore et al., 2013; Grand-Clement et al., 2014). Of five methods for estimating river loads reviewed by Walling and Webb (1985), method five used a discharge weighted mean
concentration rather than a time weighted mean concentration, as the latter may underestimate discharge weighted mean values. As DOC concentrations in particular are closely related to discharge (Clark et al., 2007; Grand-Clement et al., 2014) a discharge weighted mean was considered most appropriate. Method five thus allows the variation in concentration at different discharge levels to be included. This method has been used where the sampling strategy has focussed on regular sampling rather than storms (Dinsmore et al., 2010, 2013) as long as there is a continuous discharge record (Hope et al., 1997). It is also important to have a sampling pattern spread evenly across the year and across a wide range of discharges when calculating annual exports using method five (Smith, 2015), to avoid overestimating (i.e., by sampling only in summer when DOC concentrations are higher) or, underestimating (by only sampling in the winter). As sampling in this study was undertaken across all seasons and during a wide range of discharge conditions, method five was considered an appropriate choice.

5.2.6 DOC hysteresis and cumulative DOC export
To look specifically at concentration change patterns during storms, we plotted discharge against DOC concentration. Hysteresis occurs when different DOC concentrations are found at the same discharge on the rising and falling limbs of a hydrograph (C. Evans et al., 1999). Hysteresis has been observed in many watercourses during storms (Vinjili, 2012; Smith, 2015) and it can give an indication as to the dominant stream water source during storm events. The patterns observed tend to follow clockwise or anticlockwise loops (Evans and Davies, 1998), although occasionally figures of eight are also observed (Williams, 1989). Hysteresis results here were described in terms of the classification used by Evans and Davies (1998). This model describes the relative contributions of groundwater, pore water and event surface runoff to stream flow, based on the shape of stream water DOC response to the storm peak in discharge (Figure 5.4).

Cumulative DOC export was calculated on a daily basis between 1st October and 31st December (i.e., autumn) in both 2014 and 2015 to specifically investigate the effect of storm events on DOC export. Autumn was chosen due to having the highest seasonal DOC exports. Mean discharge was calculated for all cumulative periods (i.e., 1, 2, 3….to 92 days) from 1st October 2014 and cumulative export was calculated for each day in the season, using Equation 5.1.
Figure 5.4: Hysteresis loops showing changes in concentration and discharge during storm events. The shape of the pattern and direction (in time) indicate the relative contributions of groundwater (base flow), porewater and surface runoff (event water) to stream flow. Adapted from Evans and Davies, 1998.

5.2.7 Statistical analyses
All statistical analyses were done using RStudio (Version 0.98.501, R Core Team, 2016). Monthly aquatic carbon concentrations and exports were compared between catchments in a before-after-control-impact design using linear mixed models (LMMs) and generalised linear mixed models (GLMMs) with the functions *lme* (package *nlme*, Pinheiro et al., 2016) and *glmmPQL* (package *MASS*, Venebles and Ripley, 2002) respectively. As simpler models, LMMs were first used and where data could not be modelled using LMMs (poor model fit), they were modelled using GLMMs by varying the error family and link functions until the best model fit was found. Appropriateness of model fit was checked by normality and homoscedasticity of residuals along with checks for autocorrelation (Crawley, 2007; Zuur et al., 2011). Data were modelled both as transformed (LOG10(x+1)) and untransformed to look for best fit.

The data were split into two periods pre-restoration (October 2013–October 2014) and post-restoration (November 2014 – December 2015). The post-restoration period thus began when felling started and included both the management period and the following four months. GLMs had one factor representing catchment type, one factor representing period (pre- or post-restoration) and the interaction term catchment*period. To account
for repeated measures over time, “sampling season number” e.g. Spring 2014 was added as a random intercept (compound symmetry). For DOC and DIC, monthly mean concentrations and exports were assigned to a season, whereas for POC, seasonal (mean) concentrations and exports were used in the model as only one sample per month was collected. For this reason, total carbon exports were also modelled on a seasonal timescale.

If interaction terms were significant in the model summary, they were followed with a posteriori comparison (function lsmeans, package lsmeans, Lenth, 2016) to look for significant differences between catchments in the pre- and post- restoration periods. Similarly, if the factor “catchment type” was significant (across the whole study), the differences were tested using lsmeans.
5.3. Results

5.3.1 Precipitation and flows
Precipitation totals (on the bog catchment) varied across all seasons (Table 5.2) with October to December 2014 being the wettest season (306.5 mm) and July to September 2015 being the driest one (121.6 mm). Precipitation also varied between years, with 2014 being the wettest by 330 mm. Discharge varied considerably with several large storm events occurring at similar times across all three catchments (Figure 5.5). The restoration catchment exhibited the highest total annual discharge (as mm runoff) in 2014, while in 2015 the open bog catchment was highest.

The total annual discharge was similar between 2014 and 2015 in both the restoration and afforested catchments (Table 5.2), while in the bog catchment, there was a large increase between 2014 and 2015 in both the total annual discharge (40.9% increase), despite the lower precipitation.

Runoff to rainfall ratios were seasonally variable across all catchments. On an annual basis, ratios were lower in 2014 in all catchments and increased in 2015. Over the course of the calendar year in 2015, the runoff to rainfall ratio exceeded 100% in the restoration and open bog catchments.

Air and stream temperatures were similar and varied seasonally (Figure 5.6). Mean air temperature in 2014 was slightly warmer than in 2015 (Table 5.2).
Table 5.2: Seasonal and annual statistics for mean and total stream discharge, runoff, precipitation, number of storms sampled and air and stream temperature. Yellow shading highlights spring and summer seasons.

<table>
<thead>
<tr>
<th>Period</th>
<th>Mean discharge (L s$^{-1}$)</th>
<th>Total discharge (m$^3$)</th>
<th>Total discharge - runoff (mm)</th>
<th>Runoff / Preciptation (%)</th>
<th>Precipitation total (mm)</th>
<th>Storms sampled</th>
<th>Mean air temperature</th>
<th>Mean stream temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>restoration afforested bog</td>
<td>restoration afforested bog</td>
<td>restoration afforested bog</td>
<td>restoration afforested bog</td>
<td>restoration afforested bog</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oct - Dec 13</td>
<td>260.5 121.3 66.9</td>
<td>1078711 948179 77152</td>
<td>261.8 240.4 104.2</td>
<td>124.1 114.0 49.4</td>
<td>210.9</td>
<td>0</td>
<td>4.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Jan - Mar 14</td>
<td>74.4     84.9       9.6</td>
<td>585041     652728 71359</td>
<td>142.0 165.5 96.4</td>
<td>52.8 61.5 35.8</td>
<td>269.0</td>
<td>3</td>
<td>3.9</td>
<td>3.7</td>
</tr>
<tr>
<td>Apr - Jun 14</td>
<td>55.0     43.3       9.7</td>
<td>393230     336906 72815</td>
<td>95.4 85.4 98.3</td>
<td>38.5 34.4 39.6</td>
<td>248.1</td>
<td>2</td>
<td>10.7</td>
<td>9.7</td>
</tr>
<tr>
<td>Jul - Sep 14</td>
<td>93.3     47.7       19.3</td>
<td>733254     375115 146363</td>
<td>177.9 95.1 197.7</td>
<td>75.6 40.4 84.0</td>
<td>235.2</td>
<td>1</td>
<td>14.8</td>
<td>12.1</td>
</tr>
<tr>
<td>Oct - Dec 14</td>
<td>168.8     105.4       29.2</td>
<td>1330023    828721 222190</td>
<td>322.7 210.1 300.1</td>
<td>105.3 68.5 97.9</td>
<td>306.5</td>
<td>2</td>
<td>6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>Jan - Mar 15</td>
<td>182.1     118.5       31.9</td>
<td>1598328    911077 236842</td>
<td>387.8 231.0 319.9</td>
<td>188.7 112.4 155.7</td>
<td>205.5</td>
<td>1</td>
<td>3.7</td>
<td>3.1</td>
</tr>
<tr>
<td>Apr - Jun 15</td>
<td>82.8     47.7       17.5</td>
<td>583527     370554 131527</td>
<td>141.6 93.9 177.6</td>
<td>73.7 48.9 92.4</td>
<td>192.2</td>
<td>2</td>
<td>7.3</td>
<td>8.0</td>
</tr>
<tr>
<td>Jul - Sep 15</td>
<td>31.1     30.1       14.7</td>
<td>244607     229539 111844</td>
<td>59.4 58.2 151.1</td>
<td>48.8 47.9 124.2</td>
<td>121.6</td>
<td>4</td>
<td>11.5</td>
<td>11.2</td>
</tr>
<tr>
<td>Oct - Dec 15</td>
<td>109.6     80.2       32.6</td>
<td>861809     621655 247229</td>
<td>209.1 157.6 333.9</td>
<td>105.0 79.1 167.6</td>
<td>199.2</td>
<td>2</td>
<td>6.4</td>
<td>5.9</td>
</tr>
<tr>
<td>2014 annual</td>
<td>89.3      70.4       17.0</td>
<td>3041548    2193470 512726</td>
<td>738.0 556.1 692.5</td>
<td>69.7 52.5 65.4</td>
<td>1058.7</td>
<td>9</td>
<td>8.9</td>
<td>7.9</td>
</tr>
<tr>
<td>2015 annual</td>
<td>106.6     71.9       24.0</td>
<td>3288271    2132824 722418</td>
<td>797.9 540.7 975.7</td>
<td>111.1 75.3 135.8</td>
<td>718.5</td>
<td>8</td>
<td>7.3</td>
<td>7.1</td>
</tr>
</tbody>
</table>
Figure 5.5: Discharge time series for (a) restoration catchment (b) afforested catchment and (c) open bog catchment. Daily precipitation totals from the open bog catchment are
given in (d). Data are from start of collection period in each catchment up to 31st December 2015. Grey shaded section represents forest-to-bog restoration management period (November 2014 – August 2015).

Figure 5.6: Time series for (a) stream temperature in open bog catchment (b) air temperature from metrological station on open bog catchment. Data are from start of collection period in each catchment until 31st December 2015. Grey shaded section represents forest-to-bog restoration management period (November 2014 – August 2015).

5.3.2 Aquatic carbon concentrations and exports

5.3.2.1 DOC
Monthly DOC concentrations exhibited an underlying seasonal pattern with maximum concentrations occurring in summer and lowest levels in winter (Figure 5.7a). There was a similar trend across all three streams. DOC concentration was always higher in the restoration catchment even prior to forest-to-bog restoration, indicating clear inter-catchment differences (F=26.23, p<0.001 (effect of class). There was no significant
difference in the effect of restoration between catchments (model interaction; F=1.43, p=0.2461). However, following restoration between June 2015 to November 2015, DOC concentrations increased in the restoration catchment, but not in the control catchments. Across the whole study, the restoration catchment had significantly higher DOC concentrations than the open bog (t=6.27, p<0.0001) or afforested catchments (t=4.26, p=0.0002).

Higher DOC exports per unit area (Fig 5.7b) were often observed in the restoration catchment, even prior to restoration management. There was a similar trend with time in all catchments, with generally higher exports in autumn; the obvious exception was August 2014, when one of the largest storms recorded during this study occurred (Fig 5.5), resulting in high monthly DOC export. There was no significant effect of restoration between catchments on DOC export (interaction no significant; F=0.43, p=0.6535) which precluded any further testing. However, there were significant differences between catchments (F=4.62, p=0.0138).

The restoration catchment had significantly higher DOC export than the afforested catchment across the whole study (t=2.89, p=0.0149), while DOC export from the bog catchment was not significantly different from the other two. In 2015, annual DOC export increased from the open bog (+31.7%) and restoration catchments (+27.5%) but there was a decrease (-18.3%) from the afforested catchment compared to 2014 (Table 5.3).
Figure 5.7: Monthly mean DOC concentrations (a) and DOC exports (b) with standard errors in bog, afforested and restoration catchment streams. Standard errors for export were calculated using equations 5.2 and 5.3. Grey shaded section represents forest-to-bog restoration management period (November 2014 – August 2015). The pre-restoration period was considered December 13 to October 14; the post-restoration period November 14 to December 15.
Table 5.3: Seasonal and annual mean DOC, DIC and POC concentrations and exports for each of the three catchments; also, mean discharge, FWMCs (for DOC and DIC) and summed total aquatic carbon export are presented. As forest-to-bog restoration commenced in Nov 2014, 2014 was almost exclusively pre-restoration, while 2015 is a post-restoration year. Mean concentrations are presented ± SE, while exports are presented as seasonal or annual totals ± SE of the flux calculated using equations 5.2 and 5.3 (Dinsmore et al., 2013).

<table>
<thead>
<tr>
<th></th>
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</tr>
</thead>
<tbody>
<tr>
<td>mean DOC mg L⁻¹</td>
<td>17.67</td>
<td>22.06 ± 1.00</td>
<td>23.71 ± 1.15</td>
<td>23.73 ± 1.08</td>
<td>12.75 ± 0.34</td>
<td>24.98 ± 0.87</td>
<td>46.76 ± 0.88</td>
<td>37.70 ± 0.77</td>
</tr>
<tr>
<td>mean DIC mg L⁻¹</td>
<td>87.83</td>
<td>32.37 ± 1.21</td>
<td>68.27 ± 1.69</td>
<td>37.70 ± 0.77</td>
<td>44.27 ± 1.08</td>
<td>38.89 ± 0.44</td>
<td>29.14 ± 1.16</td>
<td>78.62 ± 4.32</td>
</tr>
<tr>
<td>mean POC mg L⁻¹</td>
<td>0.29</td>
<td>0.24 ± 0.09</td>
<td>2.92 ± 0.73</td>
<td>1.05 ± 0.33</td>
<td>0.24 ± 0.09</td>
<td>0.64 ± 0.22</td>
<td>2.51 ± 0.35</td>
<td>1.05 ± 0.33</td>
</tr>
<tr>
<td>mean DOC flux kg C ha⁻¹</td>
<td>1.44</td>
<td>0.90 ± 0.09</td>
<td>0.35 ± 0.03</td>
<td>1.17 ± 0.15</td>
<td>0.19 ± 0.01</td>
<td>0.25 ± 0.01</td>
<td>0.58 ± 0.19</td>
<td>0.58 ± 0.07</td>
</tr>
<tr>
<td>mean DIC flux kg C ha⁻¹</td>
<td>0.25</td>
<td>0.84 ± 0.34</td>
<td>0.70 ± 0.31</td>
<td>0.72 ± 0.31</td>
<td>0.34 ± 0.01</td>
<td>1.96 ± 0.75</td>
<td>2.97 ± 1.01</td>
<td>1.37 ± 0.40</td>
</tr>
<tr>
<td>mean POC flux kg C ha⁻¹</td>
<td>1.24</td>
<td>0.66 ± 0.16</td>
<td>1.10 ± 0.11</td>
<td>5.55 ± 1.82</td>
<td>0.98 ± 0.01</td>
<td>2.75 ± 1.30</td>
<td>1.87 ± 2.86</td>
<td>2.86 ± 0.20</td>
</tr>
<tr>
<td>Total Aquatic C flux kg C ha⁻¹</td>
<td>90.51</td>
<td>33.93 ± 1.22</td>
<td>62.83 ± 0.83</td>
<td>95.99 ± 4.18</td>
<td>45.69 ± 1.08</td>
<td>41.89 ± 1.37</td>
<td>31.59 ± 3.09</td>
<td>82.06 ± 4.33</td>
</tr>
<tr>
<td>mean flow L s⁻¹</td>
<td>260.54</td>
<td>74.37</td>
<td>123.26</td>
<td>168.76</td>
<td>108.64</td>
<td>82.76</td>
<td>31.12</td>
<td>109.64</td>
</tr>
</tbody>
</table>

### DOC flux kg C ha⁻¹

<table>
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<tr>
<th></th>
<th>Apr - Jun 14</th>
<th>Jul - Sep 14</th>
<th>Oct - Dec 14</th>
<th>Jan - Mar 14</th>
<th>Apr - Jun 15</th>
<th>Jul - Sep 15</th>
<th>Oct - Dec 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC flux kg C ha⁻¹</td>
<td>21.92</td>
<td>23.71</td>
<td>28.62</td>
<td>18.46</td>
<td>23.98</td>
<td>20.03</td>
<td>20.55</td>
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<tr>
<td>DOC mg L⁻¹</td>
<td>85.70</td>
<td>32.37</td>
<td>44.27</td>
<td>24.81</td>
<td>48.21</td>
<td>29.03</td>
<td>37.70</td>
</tr>
<tr>
<td>DOC flux kg C ha⁻¹</td>
<td>0.44</td>
<td>0.90</td>
<td>0.19</td>
<td>0.66</td>
<td>0.77</td>
<td>0.51</td>
<td>0.58</td>
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<tr>
<td>DOC mg L⁻¹</td>
<td>2.03</td>
<td>2.45</td>
<td>2.77</td>
<td>2.16</td>
<td>2.75</td>
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### DIC flux kg C ha⁻¹

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<th>Oct - Dec 14</th>
<th>Jan - Mar 14</th>
<th>Apr - Jun 15</th>
<th>Jul - Sep 15</th>
<th>Oct - Dec 15</th>
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<tbody>
<tr>
<td>DIC flux kg C ha⁻¹</td>
<td>21.92</td>
<td>23.71</td>
<td>28.62</td>
<td>18.46</td>
<td>23.98</td>
<td>20.03</td>
<td>20.55</td>
</tr>
<tr>
<td>DIC mg L⁻¹</td>
<td>85.70</td>
<td>32.37</td>
<td>44.27</td>
<td>24.81</td>
<td>48.21</td>
<td>29.03</td>
<td>37.70</td>
</tr>
<tr>
<td>DIC flux kg C ha⁻¹</td>
<td>0.44</td>
<td>0.90</td>
<td>0.19</td>
<td>0.66</td>
<td>0.77</td>
<td>0.51</td>
<td>0.58</td>
</tr>
<tr>
<td>DIC mg L⁻¹</td>
<td>2.03</td>
<td>2.45</td>
<td>2.77</td>
<td>2.16</td>
<td>2.75</td>
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### POC flux kg C ha⁻¹

<table>
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<th>Jul - Sep 14</th>
<th>Oct - Dec 14</th>
<th>Jan - Mar 14</th>
<th>Apr - Jun 15</th>
<th>Jul - Sep 15</th>
<th>Oct - Dec 15</th>
</tr>
</thead>
<tbody>
<tr>
<td>POC flux kg C ha⁻¹</td>
<td>21.92</td>
<td>23.71</td>
<td>28.62</td>
<td>18.46</td>
<td>23.98</td>
<td>20.03</td>
<td>20.55</td>
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<tr>
<td>POC mg L⁻¹</td>
<td>85.70</td>
<td>32.37</td>
<td>44.27</td>
<td>24.81</td>
<td>48.21</td>
<td>29.03</td>
<td>37.70</td>
</tr>
<tr>
<td>POC flux kg C ha⁻¹</td>
<td>0.44</td>
<td>0.90</td>
<td>0.19</td>
<td>0.66</td>
<td>0.77</td>
<td>0.51</td>
<td>0.58</td>
</tr>
<tr>
<td>POC mg L⁻¹</td>
<td>2.03</td>
<td>2.45</td>
<td>2.77</td>
<td>2.16</td>
<td>2.75</td>
<td>1.05</td>
<td>1.05</td>
</tr>
</tbody>
</table>
5.3.2.2 POC and DIC

There were no significant effects of catchment or restoration on seasonal mean POC concentrations. However, in the restoration catchment annual mean concentrations doubled in 2015, compared to 2014, while in the control catchments annual mean POC concentrations decreased in 2015 (Table 5.3). POC export was not significantly affected by restoration, but varied between catchments (F=4.68, p=0.0314). Across the whole study period, the bog catchment exported significantly more POC than the afforested catchment and POC export followed the order: open bog catchment > restoration catchment > afforested catchment. POC export from afforested catchment decreased in 2015, while the other catchments were similar in both years.

There were no significant effects of restoration on DIC concentration or export, although there were significant inter-catchment differences in both measures (DIC concentration: F=5.72, p=0.0054; DIC export: F=29.10, p<0.0001). Monthly mean DIC concentrations were significantly higher in the bog control catchment than in the afforested catchment across the whole study (Figure 5.8a). Concentrations of DIC were variable throughout the two-year period and peak concentrations occurred in summer and autumn. DIC exports were from the bog catchment (with the largest standard errors also) were significantly higher than both the restoration and afforested catchments (Figure 5.8b). Monthly DIC export from the bog catchment was significantly higher than in the restoration catchment post-restoration (F = 4.79, p = 0.0000). The largest DIC exports occurred in autumn and winter.
Figure 5.8: Monthly mean DIC concentrations (a) and DIC exports (b) with standard errors in bog, afforested and restoration catchment streams. Standard errors for export were calculated using equations 5.2 and 5.3. Grey shaded section represents forest-to-bog restoration management period (November 2014 – August 2015). The pre-restoration period was considered December 13 to October 14; the post-restoration period November 14 to December 15.
5.3.2.3 Total carbon export
Aquatic carbon export was dominated by DOC, with this component comprising 84% to 95% of the total annual aquatic C export. Seasonally, the proportion varied from 75% to 98% of total export, with the lowest proportions occurring in the bog catchment (Table 5.3). Therefore, total aquatic carbon export tended to follow (closely) the same seasonal trend as DOC export, with the largest total carbon exports occurring in autumn (October-December 2015). POC exports were larger than for DIC, contributing to between 4% and 12.5% of the annual total carbon export, and seasonally, between 1% and 23% of total carbon export. DIC exports were <4% of the annual total carbon export, but seasonally, they contributed up to 10%.

Total carbon export was not impacted by restoration as such but as expected from patterns in DOC, DIC and POC, there were significant differences between catchments across the whole study (F=19.41, p=0.0002). The afforested catchment had significantly lower total carbon export than both the bog and restoration catchments, which were not significantly different from each other. Both in 2014 and 2015, the largest total carbon export was from the restoration catchment. The afforested and open bog catchments had similar total carbon export in 2014 but not 2015 (Table 5.3).

5.3.3 DOC and DIC concentrations and export during storm events
The effect of storm events on DOC and DIC concentrations and instantaneous exports was compared between catchments and seasons (Figures 5.9-5.12). In general, storm events caused large increases in DOC export as discharge rose. This change also depended on concentration trends. DIC exports often changed very little during storms as concentration decreased as discharge increased. Four storm events are presented here to compare trends in concentration and export between catchments, seasons and years (pre- and post-restoration). These consisted of a late spring and early summer storm (4th June 2014 and 7th July 2015) and two autumn storms (6th October 2014 and 16th November 2015). Summaries of precipitation, discharge and DOC exports are given for the restoration catchment in Table 5.4.
Table 5.4: Summary of precipitation, discharge and DOC export in two summer and two autumn storm events for the restoration catchment. A summary of all storm events sampled in each catchment is given in Appendix 5.2.

<table>
<thead>
<tr>
<th>Storm</th>
<th>3 day antecedent precipitation (mm)</th>
<th>Event precipitation (mm)</th>
<th>Initial discharge (L s⁻¹)</th>
<th>Peak discharge (L s⁻¹)</th>
<th>DOC export (mg C ha⁻¹ s⁻¹)</th>
<th>DOC concentration (mg L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Initial</td>
<td>Peak</td>
<td>Initial</td>
<td>Peak</td>
<td>Initial</td>
<td>Peak</td>
</tr>
<tr>
<td>4th June 2014</td>
<td>0.76</td>
<td>16.49</td>
<td>38.4</td>
<td>697</td>
<td>2.67</td>
<td>55.7</td>
</tr>
<tr>
<td>6th October 2014</td>
<td>3.81</td>
<td>44.45</td>
<td>18.8</td>
<td>1792</td>
<td>0.5</td>
<td>121.8</td>
</tr>
<tr>
<td>7th July 2015</td>
<td>2.80</td>
<td>13.2</td>
<td>26.2</td>
<td>239</td>
<td>3.17</td>
<td>28.3</td>
</tr>
<tr>
<td>16th November 2015</td>
<td>12.80</td>
<td>18.4</td>
<td>169.8</td>
<td>674</td>
<td>17.8</td>
<td>63.0</td>
</tr>
</tbody>
</table>

Summer storms (Figure 5.9 and 5.10) were important as DOC concentrations were often higher than in other seasons, with the potential to export large quantities of DOC under high discharge conditions. In the storm of 4th June 2014, (pre-restoration) DOC concentrations increased during the storm in all three catchments, with the smallest increase seen in the bog catchment (Figure 5.8). Following restoration, the storm of 7th July 2015 generated little change in DOC concentrations in the restoration catchment (Figure 5.10). However, in the afforested and open bog catchments DOC concentrations increased with discharge. DIC concentrations decreased during storms in both years in all three catchments.

The highest seasonal DOC exports were seen in autumn through a combination of high discharges and high concentrations (Table 5.3). Therefore, it was important to understand DOC dynamics in autumn storms. DOC concentrations increased during the October 2014 storm, but not in the November 2015 storm, while DIC concentrations decreased during both autumn storms (Figures 5.11, 5.12). DOC concentrations were lower in the two autumn storms than in the summer storms, except in the restoration catchment. Here, in the November 2015 storm, DOC concentrations were higher than in summer 2014 storms.

In all four storms, there were large differences in the peak discharge between the three catchments, with the restoration catchment showing the highest peak discharge and the greatest discharge increase during the storm. As this catchment had the highest DOC concentrations also, the highest instantaneous DOC exports were in the restoration catchment. In the restoration and bog control catchments the instantaneous DOC export...
followed the discharge closely, while in the afforested catchment the export followed concentration more closely.

Figure 5.9: DOC and DIC dynamics during a storm on 4th June 2014 (spring, pre-restoration), showing discharge, concentrations and instantaneous exports of (a) DIC in restoration catchment, (b) DIC in afforested catchment, (c) DIC in open bog catchment, (d) DOC in restoration catchment, (e) DOC in afforested catchment, (f) DOC in open bog catchment.
Figure 5.10: DOC and DIC dynamics during a storm on 7th July 2015 (summer, post-restoration), showing discharge, concentrations and instantaneous exports of (a) DIC in restoration catchment, (b) DIC in afforested catchment, (c) DIC in open bog catchment, (d) DOC in restoration catchment, (e) DOC in afforested catchment, (f) DOC in open bog catchment.
Figure 5.11: DOC and DIC dynamics during a storm on 6th October 2014 (autumn, pre-restoration), showing discharge, concentrations and instantaneous exports of (a) DIC in restoration catchment, (b) DIC in afforested catchment, (c) DIC in open bog catchment, (d) DOC in restoration catchment, (e) DOC in afforested catchment, (f) DOC in open bog catchment.
Figure 5.12: DOC and DIC dynamics during a storm on 16\textsuperscript{th} November 2015 (autumn, post-restoration), showing discharge, concentrations and instantaneous exports of (a) DIC in restoration catchment, (b) DIC in afforested catchment, (c) DIC in open bog catchment, (d) DOC in restoration catchment, (e) DOC in afforested catchment, (f) DOC in open bog catchment.
5.3.4 DOC and discharge hysteresis

In the restoration catchment, six storms showed evidence of DOC hysteresis during the sampling period (Figure 5.13). These varied in terms of concentration and discharge changes but all were anticlockwise and formed at least partial loops. There were also a range of DOC concentration changes within the storms from <2 mg L\(^{-1}\) to 20 mg L\(^{-1}\). In the afforested catchment, three hysteresis loops were observed (Figure 5.14), as fewer storms were sampled on both rising and falling limbs. The afforested catchment showed two clockwise loops and one anticlockwise, all demonstrated less than a 3 mg L\(^{-1}\) variation in DOC concentrations. From the open bog catchment, there were four observations of hysteresis, three of which were in a clockwise direction (Figure 5.15). On 18\(^{th}\) Aug 2015 an anticlockwise loop with a figure of eight cross over around the peak discharge period was found. The range of DOC concentrations in the hysteresis loops was generally larger than in the afforested catchment (i.e., ≥ 6 mg L\(^{-1}\)).

Figure 5.13: DOC hysteresis loops from the restoration catchment in both pre-restoration and post-restoration phases. Arrows show direction of hysteresis with time through the storm event, for six different events (a-f).
Figure 5.14: DOC hysteresis loops from the afforested catchment. Arrows show direction of hysteresis with time through the storm event, for three different events (a-c).

Figure 5.15: DOC hysteresis loops from the open bog catchment. Arrows show direction of hysteresis with time through the storm event, for four different events (a-d).
5.3.5 Quantitative effect of storms on DOC export

Cumulative DOC export, calculated from October to December 2014 (Figure 5.16 a-c), was similar in the afforested and bog catchments. They both exported ~50 kg C ha$^{-1}$ during the three-month period while the restoration catchment exported almost double this at ~90 kg C ha$^{-1}$, with a much steeper trend of cumulative export throughout. During the same period in 2015, the ratios of each changed (bog +4, afforested -16, restoration -10 kg C ha$^{-1}$), although the restoration catchment still had the steepest trend in cumulative export (Figure 5.16 d-f). Noticeable step increases occurred in export when there were storms and large discharge increases.

The largest steps (i.e., short term increases in export) corresponded to the largest storms with the highest peak flows which caused a greater increase in mean discharge (used in the export calculation). The largest storm peak discharge occurred between the 7$^{th}$ and 8$^{th}$ October 2014 in all three catchments, which caused export to increase by 6.8, 2.6 and 5.3 kg C ha$^{-1}$ from the restoration, afforested and bog catchments respectively. This was the largest daily increase in cumulative export during the season and represented 7.6% (restoration), 5.4% (afforested) and 10.3% (bog) of the 2014 seasonal flux. In 2015 the rate of cumulative export increased from mid-November when the first storm events of the season began.

Two storms events were sampled in each season, with additional samples collected in the monthly and ad-hoc sampling (black triangles in Fig 5.16 a-f). Cumulative export was therefore based on these samples only, making the assumption that concentrations did not change in between.

The largest daily exports corresponded to the largest mean daily specific discharges (discharge per hectare of catchment; Figure 5.16 g-l). In autumn 2014, the slope of the mean daily discharge versus the daily DOC export was similar for both the restoration (Figure 5.16 g) and the afforested catchments (Figure 5.16 h), suggesting the same rise in discharge in either catchment would cause a similar rise in DOC export. In 2015, the slope was steeper in the restoration catchment suggesting that the same rise in discharge would now cause a greater increase in DOC export. The bog catchment graph (Figure 5.16 i,l) generally had a similar range in specific discharge to the restoration catchment but a less steep slope, which was similar in both years.
Figure 5.16: (a - f) Cumulative DOC export (●), discharge, (●) and DOC concentrations (▲) from 1st October 2014 to 31st December 2014 in (a) restoration catchment, (b) afforested catchment and (c) open bog catchment and from 1st October 2015 to 31st December 2015 in (d) restoration catchment, (e) afforested catchment and (f) open bog catchment. (g - l) relationship between mean daily specific discharge (weighted by catchment area) and daily DOC export (both square root transformed) in October-December 2014 (g) restoration catchment, (h) afforested catchment and (i) open bog catchment and in October-December 2015 in (j) restoration catchment, (k) afforested catchment and (l) open bog catchment.
Figure 5.16: continued
5.4. Discussion
In general, in the first year following forest-to-bog restoration we found no statistically significant changes in concentrations or export of aquatic carbon species. However, there were some interesting temporal concentration changes and trends in annual exports, which may indicate some more subtle effects.

5.4.1 DOC concentration and exports following restoration
Although there was no significant increase in DOC concentrations across the whole post-restoration period, there was evidence of a seasonal increase during summer 2015 in the restoration catchment. Here, mean DOC concentrations increased to 47 mg L\(^{-1}\), (25 mg L\(^{-1}\) in the control catchments), which was higher than any other period in the study. Other studies have found increased DOC concentrations (up to three years) post-felling and these changes occurred as an enhanced seasonal cycling (Cummins and Farrell, 2003b; Muller et al., 2015; Nieminen et al., 2015). The seasonal cycling of DOC is generally known to be a strong signal in peatland streams (Dinsmore et al., 2013; Ryder et al., 2014), and may be related to a thermal optimum for soil enzyme activities (Fenner et al., 2005).

Post-restoration, higher observed DOC concentrations may be linked to a combination of disturbance (due to the harvesting process) along with rising water tables (Kuikkilä et al., 2014; Nieminen et al., 2015). Rewetting of previously drained peatlands has also been found to increase DOC porewater concentrations (Clark et al., 2012), through stimulated enzyme activity, creating hotspots of DOC production through a positive feedback loop (Fenner et al., 2011). High DOC concentrations following re-wetting are then likely to decrease (to concentrations similar to undisturbed bog catchments), if given sufficient time and high water tables post-restoration, as found by Höll et al., (2009) in a 20 year post re-wetting study.

In addition, brash left on the peat surface, post-felling is as an additional source of decomposable organic material (Chapter 3.3; Palviainen et al., 2004). This can contribute to an increased DOC pool in the peat pore and surface water which is then leached into streams (Muller and Tankere-Muller, 2012). More specifically, conifer needles can also produce DOC, which can be leached by water percolating through coniferous forest litter (Hongve et al., 2000).
Our results agree with Ryder et al. (2014) who found no significant change in DOC export following felling on blanket peat in Ireland. However, several studies have found significant effects, including Nieminen (2004), who found increased DOC export following harvesting of Norway Spruce on peatland over 40% of the catchment. Although working in more mineral soils, Palviainen et al. (2014) suggested that for felling, 30% may be the critical area to minimise effects on stream chemistry. Therefore, in our study, as 12% of the catchment underwent restoration, the effects may be diluted by the undisturbed area.

When DOC export was calculated annually, in 2015 (the post restoration year) an extra 54 kg C ha\(^{-1}\) (27.5% more) were exported from the restoration catchment compared to 2014. However, DOC export from the bog catchment also increased (by 43 kg C ha\(^{-1}\); 31.7%) between 2014 and 2015. This was in spite of the fact that 2014 annual exports for the bog catchment were calculated using samples from April to December 2014 only (i.e., more concentration measures were made during periods of higher temperature), which may be expected to cause an over-estimation (Smith, 2015). The fact that there were marked increases in export from 2014 to 2015 in both the bog control and the restoration catchment suggest that something other than the management was causing the increase and explains why there was no statistical effect of restoration. With only a restoration catchment, the conclusion could have been different; thus, our results highlight the importance of having more than one control catchment (Nieminen, 2004) along with temporal replication (Stewart-oaten et al., 1986).

The highest seasonal DOC export was observed in autumn (October-December) in this study, which corresponded to periods of higher mean discharge and moderately high concentrations. High DOC export has also been observed in autumn from both afforested and open blanket bog catchments in other studies (Dinsmore et al., 2013; Ryder et al., 2014).

5.4.1.1 Comparison of DOC export values

The annual DOC exports calculated for 2014 and 2015, ranged from 110 ± 4 kg ha\(^{-1}\) (afforested catchment 2014) to 253 ± 17 kg ha\(^{-1}\) (restoration catchment 2015). These are significantly less than those calculated for similar catchments near the Dyke Forest between 2009 and 2011 when annual DOC export ranged from 403 ± 65 kg ha\(^{-1}\).
(afforested catchment) to $943 \pm 59$ kg ha$^{-1}$ (open bog catchment, Vinjili, 2012). However, from an open bog catchment in south east Scotland, average annual DOC export between 2007 and 2011 was $193 \pm 46$ kg ha$^{-1}$ (Dinsmore et al., 2013), which is similar to the data presented in this study. Generally, DOC export calculated from this study fitted well within a range of values previously reported for the UK (Table 5.4). Although DOC export does not equate to total aquatic carbon export, we have chosen to compare this, due to a greater number of studies measuring DOC than total aquatic carbon.

Table 5.5: Comparison between annual DOC exports reported from this study and elsewhere from blanket bog catchments in the British Isles. This comparison was made with DOC export as it is the major component of aquatic carbon and more studies measure DOC than total aquatic carbon.

<table>
<thead>
<tr>
<th>Catchment characteristics and management</th>
<th>Site location</th>
<th>Year</th>
<th>Annual DOC export range kg ha$^{-1}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study. Forest-to-bog restoration during study and one-year post-restoration. Range includes controls.</td>
<td></td>
<td>2014-2015</td>
<td>110 – 253</td>
<td>-</td>
</tr>
<tr>
<td>One bog, one afforested, one previously restored 2004. Forest-to-bog restoration five years prior to sampling. Forsinard, Scotland</td>
<td>Forsinard Flows NNR, Sutherland, Scotland</td>
<td>2009-2011</td>
<td>403 – 943</td>
<td>Vinjili, 2012</td>
</tr>
<tr>
<td>Drained and drain-blocked open bog catchments Reduced discharge = reduced export in blocked</td>
<td>North Pennines, England</td>
<td>2002-2003</td>
<td>46 – 52 (blocked) 172 (unblocked)</td>
<td>Gibson et al., 2009</td>
</tr>
<tr>
<td>Afforested catchment prior to felling</td>
<td>Burrishoole catchment, Newport, County Mayo, Ireland</td>
<td>2010</td>
<td>95</td>
<td>Ryder et al., 2014</td>
</tr>
</tbody>
</table>
5.4.2 Concentration and exports of other aquatic carbon species following restoration

Forest felling operations are known to cause increases in particulate matter in streams (Finnegan et al., 2014b; Palviainen et al., 2014) thus we may expect increases in POC concentrations following restoration. As there was no significant increase in POC concentration or export in the restoration catchment, this implies that drain blocks and silt traps were effective (at least to some degree). The higher POC export exhibited from the bog catchment was likely a consequence of catchment characteristics.

The lack of significant detectable change in DIC concentrations following restoration may simply be because concentrations were generally very low anyway (making it more difficult to detect significant differences), or, it may also suggest that any disturbance related changes in soil processes do not influence stream DIC concentrations. The higher DIC concentrations in the bog catchment compared to the afforested catchment suggests there could be additional DIC sources in the bog catchment. DIC can be released from carbonate weathering (Billett et al., 2007) as well as from soil organic matter derived sources (Blodau and Siems, 2012). There may well be an influence from carbonate rich groundwater in the bog catchment, as peaks in DIC occurred in June 2014, September 2014 and September-October 2015 (Figure 5.8a). These periods coincided with low discharge when a higher groundwater influence may be expected (Dawson et al., 2002; Dawson and Smith, 2007). Previously, increased DIC production as a result of microbial respiration has also been found just below the water table when compared to above it (Blodau and Siems, 2012). However, this effect was associated with afforested sites and was explained by the presence of more easily decomposable leachates and root exudates, and hence, would be less likely to explain higher DIC in the bog catchment here.

5.4.3 Total aquatic carbon export following restoration

Given there were no significant changes in total aquatic carbon export, this suggests that forest-to-bog restoration can be carried out as a management practice (at this scale; <12% catchment) without impacting on the aquatic carbon cycle in the first year post-restoration. As total aquatic carbon export was dominated by DOC export (75-98%), it tended to follow (closely) the same seasonal trend as DOC export. Increases in annual total carbon export between 2014 and 2015 in the restoration catchment (26%) appeared
to be a consequence of increasing mean discharge (19.3%) and (seasonally) increased DOC concentrations. In the bog catchment the increase in total annual carbon export (28.1%) was seemingly a consequence of a marked increase in annual mean discharge from the bog catchment (a 40.9% increase compared to 2014), as there were no marked increases in concentrations of aquatic carbon species. In line with DOC export, the largest total carbon exports occurred in autumn (October–December 2015). This period corresponded to higher mean discharge and higher DOC concentrations than in the winter period, where export tended to decrease despite high discharge, as found by Dinsmore et al. (2013).

To contextualise total aquatic carbon export within the peatland carbon cycle it is important to understand the proportion of the whole carbon budget that this represents and how it affects the strength of the catchment in terms of acting as a carbon sink or source. Recent work has enabled this comparison to be made at a site adjacent to the bog catchment. Here, the average NEE from 2008-2013 was measured to be -1140 kg C ha\(^{-1}\) yr\(^{-1}\) (Levy and Gray, 2015), showing this site to be a strong carbon sink. Total aquatic carbon export from the bog catchment in this study (taking the higher 2015 estimate of 206 kg C ha\(^{-1}\) yr\(^{-1}\)) is then equivalent to 18.1% of this quoted 2008-2013 NEE. This clearly represents a significant loss of carbon from the system, but the net carbon balance remains strongly negative (i.e., as a sink). There is currently no data available from recent restoration or afforested bog catchments in the Flow Country to contextualise aquatic carbon export from these types of catchments. Ultimately, these data will be required in order to understand the relative carbon balance prevailing at afforested, restoration and bog catchments – and thus, quantify a carbon budget for the wider flow country landscape.

5.4.4 Hydrological changes affecting carbon exports

5.4.4.1 Water balance

The large increase in discharge from the bog catchment in 2015 (40.9% mean / total annual discharge increase) contributed to an increase in export of all aquatic carbon species in 2015. However, as total precipitation (measured in the bog catchment) was actually 330 mm less in 2015 than in 2014, it appears that a more complex interaction
between discharge, precipitation patterns, water storage and catchment characteristics occurred.

The runoff to precipitation ratio was 135% for calendar year 2015 in the bog catchment and 111% in the restoration catchment. In the bog catchment, 719 mm of precipitation was recorded and 976 mm of runoff left the catchment. This first suggests that changes in water storage (within a calendar year) in the peat pore-water (sub surface) and pools (surface) are important contributors to the water budget. Secondly, it suggests that a calendar year, is not a period where the water cycle is in balance (Likens, 2013).

A water year is defined by a 12-month period that begins and ends with little inter-annual change in catchment water storage and can be identified by finding a 12-month period with the greatest correlation between precipitation and stream flow (Likens, 2013). This has been defined by others as 1st June to 31st May (Likens, 2013), or 1st October to 30th September (Holden et al., 2006). Here, it was not possible to determine a calendar year, having only two calendar years of data; although neither of the above periods for the years 2014/2015 had less precipitation than runoff for the bog catchment.

On a seasonal (3-month) basis, there was clear temporal variation in the runoff to precipitation ratios, which were lower in spring and summer in the afforested and restoration catchments, but less seasonally defined in the open bog catchment (Table 5.2). Generally, in summer months, higher evaporation (not measured) can decrease the runoff to precipitation ratio (Holden et al., 2006) and the withdrawal of storage (pore) water can contribute to streamflow (M. Evans et al., 1999). At other times, seasonal ratios were often more than 100%, which has commonly been observed by others working in blanket bog and afforested catchments (M. Evans et al., 1999; Likens, 2013). This again reflects the relative changes in precipitation, water storage and evapotranspiration. In months where runoff exceeded precipitation, it appears storage (pore water) and precipitation were both contributing to streamflow, with little evapotranspiration.

Similarly, there can be inputs from surface water storage, which adds to the complexity of the peatland water balance. Rain fed peatland pools have outflows leading to small streams or ditches e.g. (Turner et al., 2016). Therefore, at times of high rainfall, pools could also act to enhance water inputs to a catchment. In the bog catchment, peatland pools were situated on the edge of the catchment boundary, thus there is a possibility of
having a larger catchment area (on a temporary basis), than is traditionally measured using digital elevation models and used in our calculations.

This effect could also be enhanced by the presence of peat pipes, which are quite ubiquitous in blanket peatlands (Holden and Burt, 2002). These can be long (> 150m) and difficult to trace and could therefore bring water into the catchment from outside the boundaries (Jones, 1997; Holden and Burt, 2002). This may also happen on a variable nature, as pipes are often a route by which water escapes at times of high rainfall and therefore could be a seasonal/ temporary route (Holden and Burt, 2002).

Another water input into the catchment, is peatland fog (Price, 1992a). As fog is not recorded as precipitation by the rain gauge, it may contribute to the high runoff ratios at times, where the precipitation/runoff balance appears negative.

We also made the assumption, that precipitation measured in the bog catchment was representative of that which fell in the restoration and open bog catchments, as only one rain gauge was available. As, there was a 6-8 km distance between catchments (restoration and bog), it is possible that precipitation amounts varied across this distance.

A longer precipitation record (to determine the hydrological year), measuring evapotranspiration, the determination of additional water inputs (pipes and pools) and consideration of fog, may therefore help to complete the water balance for this study.

**5.4.4.2 Precipitation patterns**

Precipitation patterns throughout the two-year study period can also be used to help interpret the runoff / precipitation ratios measured for the calendar years 2014 and 2015. In 2015, monthly precipitation was less than 2014 in all months except January, June and November (Appendix 5.3a). However, in 2015, there were more rain days (>0 mm precipitation) in seven months out of 12, including a continuous spell of more rain days per month from March through to July (Appendix 5.3b). This further resulted in higher mean discharge in nine out of 12 months in 2015 (Appendix 5.3c). In bog catchments generally, water table depth (WTD) is closely related to streamflow fluctuations (Price, 1992b) and overland runoff is generated by saturation excess (M. Evans et al., 1999) .

The higher number of rain days, particularly during summer 2015, resulted in slightly higher water tables (open bog plots; chapter 3). This may have helped prevent drought conditions, increasing the amount of saturation excess runoff (M. Evans et al., 1999).
Higher water tables and wet antecedent conditions, can result in more rapid discharge generation and greater surface runoff (Daniels et al., 2008), which could contribute to the higher runoff in 2015. Furthermore, there were lower summer mean air temperatures in 2015 (Table 5.2), which would result in lower evapotranspiration (Heggen, 1996), helping to maintain higher water tables.

Conversely, in 2014, the months with fewer rain days could have induced drought periods, especially in June and July. Additionally, higher mean air temperatures may have increased evapotranspiration. However, there is a limit to which evaporation can lower WTD, if capillary flows cannot meet evaprotanspiration demand. During drought periods the areas contributing to runoff generation have been found to be variable and somewhat unpredictable in their connections to generating runoff (Richardson et al., 2012). This concurs with evidence that during dry antecedent conditions, the response to precipitation events can be slower, with reduced runoff (Daniels et al., 2008) and smaller peak discharges (M. Evans et al., 1999). Therefore, drought periods with drier antecedent conditions may have contributed to lower discharge in 2014 and greater water storage. As there were much smaller changes in the discharge in the other catchments between 2014 and 2015 than the bog catchment, this also suggests that the hydrology of the bog catchment was more susceptible to climatic changes, such as precipitation patterns and temperature.

5.4.4.3 Canopy interception of precipitation

In the afforested catchment and the restoration catchment before tree harvesting, increased evapotranspiration through interception of precipitation and transpiration by the tree canopy will reduce the amount of precipitation which flows out of the catchment (Swank and Douglass, 1974). Conversely, following restoration management and after felling, it is likely that increased surface runoff would occur, increasing catchment discharge (Rosén et al., 1996; Nieminen, 2004). If we assume that similar precipitation occurred in all three catchments, then tree removal in 2015 in the restoration catchment could also help explain the slight rise in total annual discharge (compared to 2014), while there was a slight fall in total annual discharge between 2014 and 2015 in the afforested catchment. In one study, canopy interception has been found to account for 11% of annual precipitation falling on the forest canopy in a mixed coniferous and deciduous forest (Xiao et al., 1998).
Canopy interception can also affect the chemistry of water reaching the ground and infiltrating into the peat porewater (Likens, 2013). DOC leaching from Spruce canopy throughfall (Germany) has been found to contribute up to 13.8 mg L\(^{-1}\) (>50% stream DOC in our afforested catchment; Guggenberger and Zech, 1993); however, this wasn’t measured at our sites. This may be an additional factor which resulted in the afforested and restoration catchments in our study having higher DOC concentrations than in the open bog. Precipitation DOC collected on the open bog was measured to have an average of 0.6 mg L\(^{-1}\) of DOC (monthly sampling 2015). As such, in open bog areas at least, precipitation contributed only a very small fraction of total DOC to the drainage streams.

5.4.5 Importance of storm events in terms of concentration and export of aquatic carbon

5.4.5.1 Patterns of DOC and DIC concentration and instantaneous export

Here, increased DOC concentrations were often observed during storm events, as also noted by Eimers et al. (2008) in upland streams. These storm related increases in DOC concentration also contributed to an overall increase in DOC export (Figures 5.9-5.12). For this study, in general DOC concentrations increased during storms within the summer and autumn seasons. This has been found in other studies focussing on storm event DOC (Buffam et al., 2001; Grayson and Holden, 2012).

In autumn (~November) there was a switch in patterns and from then on DOC concentrations decreased or remained constant during storms, which continued through winter and into the following spring. This concurs with Koelher et al. (2009) who found that in colder periods, DOC concentrations were independent of flow in a blanket bog stream. At low temperatures there is less DOC production (Clark et al., 2009), so, during winter flow through surface porewater appeared not to contribute additional DOC to the stream, compared to surface runoff.

Therefore, there are also seasonal effects of storms on DOC export, with summer storms contributing relatively more to export (Smith, 2015) due to higher prevailing DOC concentrations (Koehler et al., 2009). Overall, not sampling storms in a particular season/regularly could have led to skewed estimates of the total annual export, as concluded by Clark et al. (2007).
Although post-restoration DOC concentrations were (NS) higher in the restoration catchment, it would be expected that seasonal patterns would still hold (Cummins and Farrell, 2003b) and thus patterns of concentration change during storm events. This was generally true, as in summer storms the same seasonal patterns in DOC concentration were found pre- and post-restoration in the in the restoration catchment. However, during one summer storm (07 July 2015; post-restoration) DOC concentrations in the restoration catchment showed little change and concentrations were high (~50 mg L\(^{-1}\)) at the storm onset. This was contrary to the patterns observed in the control catchments and other summer storms sampled during this study. The lack of change in DOC concentration during this particular summer storm in the restoration catchment suggests that pre-event water (deep pore water) and event water (storm runoff and surface pore water) were all high in DOC. It further suggests that the DOC pool was not depleted during the storm (Smith, 2015), which could be due to enhanced DOC production, stimulated by rewetting within the peat (Fenner et al., 2011) or brash decomposition (Muller et al., 2015).

As such, our study indicates a possible effect of forest-to-bog restoration on DOC delivery during storm events. However, in three other events sampled during the summer/autumn 2015 period, increased DOC concentrations were found. Thus the observation in the July 2015 event may be an anomaly, rather than an actual management effect. Only one other study has investigated DOC export during storm events following felling on blanket peat and they did not report any effects on storm event DOC delivery (Ryder et al., 2014).

Despite large increases in discharge, the effect of storms on DIC was generally to induce a decrease or little change in instantaneous DIC export, regardless of season or forest-to-bog restoration (Figures 5.9-5.12). This was due to the relatively large decrease in DIC concentration seen during storm event (as found by Dinsmore and Billett, (2008) when measuring dissolved CO\(_2\)). In our study, DIC concentrations decreased during storm events as both pore water and surface runoff were in contact with largely organic matter. Thus, during storms any mineral influence from the groundwater component of stream water would have been diluted by surface runoff and pore water entering the stream (Vinjili, 2012; Muller et al., 2015).

### 5.4.5.2 DOC hysteresis patterns and cumulative export

Hysteresis provided an insight into the processes that supply DOC - in terms of mixing of the various stream water components (Evans and Davies, 1998) and into seasonal differences in storm export (Aulenbach et al., 2014). In our study, wider loops with a
larger DOC range were observed in summer or autumn storms and were also associated with generally higher DOC concentrations (Figures 5.13, 5.15). In winter storms, with small DOC concentration ranges (~2 mg L\(^{-1}\)), there was considered little difference between event runoff and pore water DOC concentrations (i.e., two of the stream water mixing components during storms).

The restoration catchment showed mainly anticlockwise hysteresis loops. Anticlockwise loops indicated that the pore water component was higher in DOC than the event surface water, which reached the stream first, causing lower concentrations on the rising limb (Evans and Davies, 1998). Therefore, porewater was the main influence on DOC concentrations during the storm. This resulted in a steady increase in DOC concentrations during storm events (Figures 5.9d, 5.11d). In the 19\(^{th}\) March 2014 storm, there was a small figure of eight crossing over in a clockwise direction indicating that there may have been an earlier influence of higher DOC porewater prior to peak discharge (Smith, 2015) (Smith, 2016). Figure of eight loops are widely reported (Williams, 1989) and are associated with multiple processes during the same event (Smith, 2015). As anticlockwise hysteresis patterns were observed in both pre- and post-restoration period, this suggests DOC delivery during storms was largely unaffected by restoration.

In contrast, the open bog catchment showed clockwise loops which corresponded to higher DOC in the event surface runoff which reached the stream before the porewater (Smith, 2015). Open bog pore water may be lower in DOC (than event runoff water), as the decomposition processes producing DOC are likely less active when compared to those in the restoration catchment. This may be a consequence of the higher water table in the bog catchment (Chapter 3; Strack et al., 2008) and it is a clear example of the influence of catchment characteristics. The lower DOC concentrations in porewater were reflected in DOC concentration trends during storm events which sometimes decreased in the falling limb of the storm (Figure 5.10f, Figure 5.11f). In the 18\(^{th}\) August 2015 event an anticlockwise loop with figure of eight cross over around the peak discharge point was found in the open bog catchment. In this case, porewater had the greatest influence on DOC concentrations. This fits with the expected seasonal DOC production patterns, as the highest stream DOC concentrations occurred in summer (Fig 5.7a) and these were then flushed from peat pore water during high rainfall events (as also noted in Koehler et al., 2009: Grand-Clement et al., 2014).
In the afforested catchment there were fewer examples of hysteresis, in part, due to a number of incomplete storm events sampled, as peak discharge in this catchment was sometimes different from the other two. Generally, all loops showed a small range of DOC concentrations with less difference between event runoff and pore water DOC concentrations than in the other catchments (Figure 5.14). The observed hysteresis was both clockwise (10th December 2014), where the event surface water was the main source of the DOC (Vinjili, 2012), and anticlockwise (7th March 2015) where pore water was higher in DOC. It is therefore plausible that hysteresis direction can change seasonally and in relation to antecedent moisture conditions (Andrea et al., 2006; Aulenbach et al., 2014).

Generally, the larger storms (Fig 5.11 – October 2014) caused higher DOC export, which has been widely observed in other studies (Grieve, 1984; Clark et al., 2007). In terms of cumulative export, the largest daily increases in DOC export occurred during the largest storm events, as observed by Ryder et al., (2014) who calculated cumulative export in a forested catchment undergoing clear felling. While the largest changes in exports and highest peak discharges were in the restoration catchment, the general pattern of step changes in export was very similar in all three catchments. Therefore, catchment characteristics strongly influenced the size of exports rather than patterns of export. A similar rise in discharge in either the restoration or afforested catchment was found to cause a similar increase in DOC export for both in autumn 2014 (Figure 5.16). In autumn 2015, that the same rise in discharge in the restoration catchment would now cause a greater increase in DOC export, which may have been a consequence of the higher DOC concentrations post-restoration.

5.4.6 Catchment size comparisons
In this study, the comparison of two similar sized catchments (restoration and afforested) is made against a much smaller open bog catchment. In doing this, it is assumed that there are similar processes influencing aquatic carbon export in all catchments. The small open bog was the best available bog control and was preferable to a much larger bog catchment (second choice), as in larger catchments there are potentially multiple/different processes controlling carbon concentrations and export (Billett et al., 2006). This is thought to be due (at least in part) to simple hydrological mixing along the catchment, as tributary streams join and contribute to losses or gains of carbon species (Dawson et al., 2004). A
study from a peatland catchment in north east Scotland found that within the upper 1.5km of headwaters of the catchment, there was a good relationship between pore water DOC and stream water DOC. Further downstream, the interconnectivity weakened due to in-stream processing of DOC and the influence of mineral soils on stream chemistry (Billet et al., 2006)

5.4.7 Consideration of total aquatic carbon budget
There were two further assumptions related to the complete aquatic carbon budget presented here. Firstly, seasonal POC export calculations were based on three samples per season from the monthly sampling regime. This means (compared to DOC and DIC) there was less chance of capturing variations in POC concentrations, which have been found to vary with temperature and discharge (Ryder et al., 2014). Although our POC sampling covered a range of discharge conditions (sampling across all seasons over two years), we did not target storm events where the largest POC exports often occur (Pawson et al., 2008). Therefore our annual POC exports may be an underestimate, compared to that measured from similar studies, which are more than double that of our annual POC exports (Dawson et al., 2002; Vinjili, 2012; Ryder et al., 2014).
Secondly, the total aquatic carbon export in this study comprises of DOC, DIC and POC, of which DOC was the major component (≥ 84% annual export). The dissolved greenhouse gases (GHG) CO₂ and CH₄ are also components of the aquatic carbon export budget (Billett and Moore, 2008). Typically, they are small components (between 1% and 5% of annual aquatic carbon export) from peatland catchments, with decreasing importance moving downstream (Dawson et al., 2002, 2004; Hope et al., 2004). They can be seasonally important, with not only downstream export but evasion to the atmosphere being the larger contribution to their significance (Dinsmore et al., 2010). For example, evasion of dissolved CO₂ from the stream surface was found to be larger than DOC export, in spring (low discharge and high temperature). This was despite the downstream export of dissolved CO₂ being less than 10% of DOC export (Dinsmore et al., 2013). However, these flux terms also have the largest errors due to uncertainties surrounding gas transfer coefficients (Dinsmore et al., 2013). Technically, dissolved CO₂ is part of the equilibrium between carbonate and bicarbonate which are the main components of DIC
(Dawson et al., 2002). However, because of the natural degassing of free CO₂ it is not measured when testing for DIC and therefore needs to be collected separately by headspace sampling and measured by gas chromatography (Kling et al., 1991; Dawson et al., 2002), which was not undertaken as part of this study. Dissolved CO₂ and CH₄ were found to be intercorrelated and both correlated with temperature and conductivity associated with groundwater (Dinsmore et al., 2013). Generally, dissolved CO₂ has been associated with older carbon from deep within the peat (Billett et al., 2007), rather than the upper layers which are more affected by disturbance; which suggests, that they may not be significantly affected by forest-to-bog restoration. However, recent work in Finland found modern dissolved CO₂ associated with root respiration below a frozen soil surface, but, there was little difference in terms of the source and age of dissolved CO₂ between drained and undrained sites (Billett et al., 2011). As dissolved GHG are a small component of downstream aquatic export (not including evasion) and they may not be affected by management, we have assumed here that they would not add a significant component to the total aquatic carbon budget calculated.

5.4.8 Implications of findings in the longer term and for management
The most important factors in determining aquatic carbon export in this study were catchment characteristics and discharge (including the effect of storms). Although there were some seasonal concentration increases in the restoration catchment (likely related to forest-to-bog restoration), there was no significant effect of restoration on concentrations of exports of aquatic carbon.

Seasonal and discharge effects on aquatic carbon may be exacerbated by climate change (Freeman et al., 2001a, 2004; Frey and Smith, 2005; Winterdahl et al., 2014; Pinsonneault et al., 2016) and other long term trends such as changing atmospheric deposition (Evans et al., 2006; Monteith et al., 2007), which are likely to impact on aquatic carbon exports (perhaps) as strongly as management change (Fleischer et al., 2016). Effects of climate change are through both increasing temperatures and changes in precipitation patterns which differ across the UK (Watts et al., 2015). Such effects were observed in the bog control catchment, where 2015 precipitation decreased by 32% but the precipitation pattern, along with lower temperatures, seemingly caused an increase in total annual discharge of 41%. If the same percentage increase in discharge had occurred across the
restoration catchment in 2015, along with the seasonally higher DOC concentrations observed this may have caused significantly higher exports than in the control catchments.

Further to this, under climate change scenarios, increasing atmospheric CO$_2$ may drive increased DOC production (Freeman et al., 2004), and climate induced changes in vegetation cover have been thought to potentially prime decomposition of organic matter (Bragazza et al., 2012b). This would likely occur due to changes in soil microbial community structure, through changes in litter chemistry and through rhizodeposition decreasing *Sphagnum* productivity (Bragazza et al., 2012b). Therefore, climate induced changes in precipitation and DOC production may potentially have a confounding effect on the long term goal of restoration of restoring the water table and native blanket bog vegetation (Holden et al., 2007b; Lunt et al., 2010) and carbon sink functioning (Artz et al., 2012).

The lack of significant changes in aquatic carbon following forest-to-bog restoration, may have been a consequence of carrying out restoration on 12% of the catchment area. Although large increases in DOC concentration and export when harvesting ≥ 40% of a forested peatland catchment (Nieminen, 2004), harvesting even just 15% of a peatland catchment area has caused increased carbon exports (Lundin, 1999). Therefore, in our study site if further restoration is carried out within the catchment while there is still the potential for increased DOC concentrations from the current restoration area, (~ 3 years post felling; Nieminen et al., 2015) aquatic carbon export may start to increase significantly, and should be monitored.

The harvesting which occurred in the restoration catchment was a mixture of standard and enhanced harvesting. As standard harvesting was stem only harvest, there were large amounts of brash left on the peat surface (a potential source of DOC and POC to streams; Muller et al., 2015). Therefore, to remove all brash may help mitigate future increases in stream DOC and POC concentrations. The use of harvesting machinery also resulted in scarring of the peat surface where vegetation was unintentionally removed leaving bare peat exposed, which may also have increased erosion along with stream DOC and POC concentrations (Holden, 2005; Lilly et al., 2005, 2009). In order to carry out forest-to-bog restoration with trees of this age (30-40yrs), it was necessary to use heavy machinery, although the very latest harvesters are low ground-pressure (Andersen et al., 2016). Damage to the peat surface was unavoidable, even though machinery drove on brash mats.
where possible and the disadvantage of removing brash, was extra passes of machinery on the peat surface.

The use of drain blocks and silt traps were seemingly effective in preventing a significant increase in POC stream concentrations. As a further measure of reducing sediment transport and retaining water in the restored area, plough furrows are to be blocked in the restoration catchment. If these act like a standard drain block then discharge can be reduced (Gibson et al., 2009), although tree removal is known to increase discharge (Rosén et al., 1996) so the net effect of forest-to-bog restoration on discharge is unknown. The effectiveness of furrow blocking in reducing aquatic export from restoration sites may therefore be an interesting future research question.

In application to the wider management of afforested peatlands across the country, the ecosystem services from a particular catchment will be an important influence on the drivers for restoration. Where a catchment is used for drinking water, increased DOC concentrations may be problematic in terms of increasing water treatment costs for aesthetic purposes (Worrall et al., 2007) or due to the potential health concerns related to disinfection bi-products (Hsu et al., 2001). Thus, this may be a disincentive for large-scale forest-to-bog restoration (at least over larger catchment areas) and a precautionary approach may be needed where downstream waters are used for drinking water supply. Where the main service is as a carbon store, the aquatic carbon export must be considered along with the NEE of the GHGs (Dinsmore et al., 2010). If aquatic carbon export is one of the main losses from a system with a small negative NEE, then it would be important for management to target aquatic losses specifically. This may be by using measures such as restoring smaller areas of a catchment or removing brash, and/or, using furrow blocking as well as drain blocking. However, this will also depend greatly on the effect of forest-to-bog restoration on GHG exchange and as shown from the bog catchment in our study, DOC export is not the limiting factor in terms of carbon sequestration. It may be that forest-to-bog restoration may cause disturbance such that increased losses of carbon occur and that until the system recovers e.g. (17 years post-restoration; Hambley, 2016), it may not be possible to retain the carbon sink functioning of the peatland (in the short term). However, as this study was conducted on a bog managed for nature conservation, management techniques focus on recovery of water table depth and *Sphagnum* re-colonisation, although this may benefit carbon sequestration as a by-product.
5.5 Conclusions
In this study there were no significant increases in aquatic carbon concentrations or export (DOC, POC or DIC) in the first year following forest-to-bog restoration. However, restoration likely caused increased DOC concentrations in the first summer (2015) and there may have been some changes in the patterns of DOC loss during storm events. The lack of significant immediate effects of forest-to-bog restoration may be a consequence of the small proportion of the catchment (12%) undergoing this management. Thus, if further restoration occurs within future years (0-3), there may be additional effects on aquatic carbon. The harvesting of stems and brash may help to mitigate any further effects (by removing a DOC and POC source), along with the blocking of plough furrows to help retain water in the restoration area. The management objective (e.g. nature conservation) will determine restoration aims and whether additional measures are required for key ecosystem services from the catchment.
6. Measuring restoration progress using pore- and surface-water chemistry across a chronosequence of formerly afforested blanket bogs

6.1 Introduction
Nutrient cycling is one of the three main outcomes commonly used in measuring restoration success, the other two being vegetation and diversity of organisms (Ruiz-Jaen and Aide, 2005). In bogs, nutrient cycling is a key control on carbon cycling (Keller et al., 2006). Therefore, if restoration brings back natural-like nutrient cycling, (e.g. Andersen et al., 2013b), it should also secure the peat carbon stocks from degradation, and help re-initiate carbon sequestration and peat formation (Bardgett et al., 2008; Juutinen et al., 2010; Bragazza et al., 2012a). As in many terrestrial systems, restoration success in bogs depends upon the recovery of both above- and belowground biogeochemical cycling of nutrients, which are linked through vegetation (Harris, 2003; Andersen et al., 2013b; Nwaishi et al., 2016) and strongly controlled by water table depth (WTD; Waddington et al., 2015).

Changes in belowground nutrient cycling are strongly linked with microbially mediated processes in the peat (Andersen et al., 2013a) which are controlled by redox-conditions, hence WTD. In turn, these changes are reflected in pore and surface water chemistry (Andersen et al., 2010; Bragazza et al., 2012b). Pore and surface water chemistry has a strong influence on bog vegetation growth and composition (Wieder et al., 1985; Vitt and Chee, 1990), but changes in vegetation also feedback on water chemistry (Eppinga et al., 2009; Bragazza et al., 2012b). Excess quantities of soluble nutrients and metals can be inhibitors to bog vegetation growth (Bubier et al., 2007) or functioning of microbial communities (Andersen et al., 2013a).

One of the primary restoration approaches used to facilitate the recovery of bog vegetation (i.e. Sphagnum) and functions is to raise the WTD to create a near surface water table similar to open bog conditions (Holden et al., 2004; Armstrong et al., 2009; Bellamy et al., 2012). A key question is how much time will be required for restoration areas to function like bog once restoration management has taken place (Hancock et al., 2014). Effectively, this depends on how indicators of success, such as WTD, nutrients and
vegetation change over time (Bubier et al., 2007; Armstrong et al., 2009; Andersen et al., 2010; Holden et al., 2011; Haapalehto et al., 2014; Parry et al., 2014).

In Finnish peatlands, formerly drained to increase forest cover, peat mineral concentrations were comparable to pristine peatlands 10 years post-restoration, suggesting recovery of nutrient cycling between peat and plants (Haapalehto et al., 2011). Although the vegetation succession had moved towards species favouring wet conditions, some species typical to pristine peatlands were still missing, thus compositional recovery of the vegetation community was still not achieved (Haapalehto et al., 2011). In a wider survey across Finland, pore and surface water chemistry was found to be approaching that of pristine sites 10 years post-restoration, with some differences in nutrient and mineral element concentrations (Haapalehto et al., 2014). The same study additionally found an indication of incomplete recovery of the hydrology, with a lowering of WTD observed adjacent to blocked ditches after five years (Haapalehto et al., 2014). Similarly, in a restored cutover bog in Canada, belowground microbial and nutrient cycling shifted towards that of natural peatlands but was not fully re-established to a degree similar to natural conditions 10 years post-restoration, and this was attributed to a fluctuating WTD (Andersen et al., 2013b). Moreover, seasonal cycling in pore and surface water chemistry (nutrients and metals) in the same restoration site (former peat harvesting), remained greater than in natural sites 10 years post-restoration (Andersen et al., 2010).

Looking specifically at dissolved organic carbon (DOC), a product of microbial decomposition (Moore, 1997), various studies of restoration on open peatlands (by drain blocking) have shown recovery of DOC to levels similar to pristine sites (Wallage et al., 2006; Höll et al., 2009). However, drain blocking has also led to modifications of DOC composition, with reported increases (Wallage et al., 2006) and decreases (Höll et al., 2009) in the dominance of darker-coloured more humified material following restoration after six and 20 years respectively. These examples from different peatland types and disturbances all point to the fact that peatland restoration is a slow, possibly multi-decadal process.

In restoration of afforested blanket bogs (Scotland), which are comparatively much more disturbed than naturally forested bogs, blocking the plough furrows and collector drains with peat dams was most successful in raising the water table and in promoting bog vegetation (Anderson, 2010); however, water levels were still lower than in undisturbed blanket bog five years after restoration. Recent monitoring of 15 year old forest-to-bog
restoration sites have shown more successful recovery of *Sphagnum* sp. on slopes <3° (Hancock et al., 2014), which was thought to be a consequence of higher water table depth (WTD) on shallow slopes.

However, there might be another factor involved in the slow recovery of the vegetation on drained and afforested blanket bogs following restoration by tree removal and drain blocking. Significant increases in pore and surface DOC, plant nutrient and mineral element concentrations occur immediately following forest-to-bog restoration (Chapter 3). Some of these changes may rise and fall within a short period and could be a consequence of the disturbance associated with restoration management. However, if they are not, and are rather a legacy effect of the plantations and associated drainage, they could last for a longer period (Gough et al., 2007; Cuddington, 2011) and contribute to impeding the recovery of key genus like *Sphagnum*. One way to test this idea is to assess the temporal dynamics of pore and surface water chemistry over several decades, to determine how long it takes before water chemistry resembles that of open bog. Given the potential for pore and surface water chemistry to reflect nutrient cycling and ecosystem recovery (Anderson, 2010; Haapalehto et al., 2014), we propose that such an assessment may be a valuable way to evaluate the recovery of forest-to-bog restoration sites. There are currently no studies of medium-long term (>5 years) changes in pore and surface water chemistry exclusively on the restoration of drained, afforested peatlands. We propose to use a space-for-time substitution (Pickett, 1989; Thomaz et al., 2012) to make a first attempt at filling this gap.

Thus the aim of this chapter is twofold:

1) Assess the differences through time in a) surface, b) shallow pore water and c) deep pore water chemistry across four restoration sites of different ages (0-17 years after restoration commenced), in comparison to afforested and open bog controls

2) To identify the pore and surface water chemistry variables which can best be used as indicators of recovery in the restoration of afforested peatlands

We hypothesised that the oldest restored sites will be closest in pore and surface water chemistry to open bog, whereas the more recent restoration sites will be more similar to afforested control sites. It is further hypothesised that concentration of DOC and plant nutrients will be key indicators of recovery in water chemistry.
6.2 Methods

6.2.1 Site description of chronosequence restoration sites (restoration between 1997 and 2015)

Forest-to-bog restoration has been carried out across the RSPB Forsinard Flows National Nature reserve since 1997, creating a series of older restoration sites with a range of ages from 17 (restoration in 1997/98) to 0 (restoration in 2014/15) years old, therefore forming a chronosequence (Figure 6.1). Most of the sites are on the east side of the River Halladale, which separates them from the Dyke forest and river, with a 15 km distance between the furthest east and west sites. Some of the older restoration sites are within the River Halladale catchment, while others drain into the Sleach, a tributary of the River Thurso.

Within four sites of different ages along the chronosequence, we selected sampling areas intended to produce a space-for-time substitution (n=3 replicates per age class). Methods used for the restoration management changed over time and depended on the size of trees and the development of specialist machinery, as planting occurred mainly occurred in the 1980s and restoration was spread over 17 years. At Talaheel (restoration in 1997/98), trees were felled by hand (chainsaw) and were lain into the furrows as they were young and small (Hancock et al., in prep.). In Lonielist (restoration in 2003/04) trees were machine felled and left in furrows i.e. felled to waste. By then the trees were bigger and did not fit in the furrows when felled: brash was sticking out. In Raphan (restoration in 2011/12), and Dyke (restoration in 2014/15) whole tree mulching has been carried out on smaller trees (<25% of area) but most stems have been harvested for timber (brash harvested in some of Dyke). The final selection of the sampling areas within each site was based on restoration technique (felled-to-waste only), location (different sub-catchment), and access (Figure 6.1; Table 6.1).

Three replicate plots from each site were chosen to match the sampling strategy in the Dyke Forest (Chapter 3), allowing the inclusion of the most recent restoration sites in this study. However, there was no fell-to-waste in Dyke Forest, so standard fell (stem only harvest) plots were included in the chronosequence, as they were the most comparable to felled-to-waste plots. Here, there were three restoration blocks, each with two plots of standard felling, thus a total of six plots were sampled. Standing forestry plantation controls (hereafter referred to as afforested) and open bog control plots situated on the Dyke side of the reserve were included in the chronosequence as the start point and
targeted end point, respectively of the restoration process (Figure 6.1). These controls were comparable to all the chronosequence sites in terms slope (Table 6.1) and vegetation cover (bog as target for recovery; forest as similar species mix and planting methods to restoration sites pre-restoration). Vegetation cover in open bog was dominated by *Sphagnum* spp. in open bog controls (38% cover), while afforested controls were dominated by other mosses (63%; *pleurocarpus* and *acrocarpus* mosses; Chapter 3.2.1; Table 3.1). Restoration sites varied in recovery towards open bog vegetation with a mean of 15% cover of *Sphagnum* sp. in the oldest restoration site (Talaheel: Hancock et al., in prep.), while Dyke (≤4% of *Sphagnum* sp. cover) was more similar to afforested controls.

### 6.2.2 Pore and surface water sampling

Pore water was sampled using piezometers, which were installed in transects of ‘nests’ as described in chapter 3.2.2. Each ‘nest’ contained one deep and one shallow piezometer, intended to sample the waterlogged and temporally aerated peat zone respectively. One transect was installed in each plot, which followed the slope direction and contained four piezometer ‘nests’ and one dipwell for measuring water table depth (WTD). Three plots were instrumented in each restoration site (and for both afforested and bog controls), except Dyke (n=6). Piezometers were emptied between four and six days prior to sample collection. Samples were collected into LDPE bottles (Nalgene) using a syringe connected to flexible PVC tubing pre-rinsed with 5 mL of sample. Surface water was sampled from collector drains (main forestry drains) in each plot (open bog plots, contained drains blocked in 1996 and 2004). Where more than one drain crossed a transect these were also sampled. For both pore- and surface-water, measurements of physico-chemical parameters (temperature, pH and conductivity) were made in the field (Chapter 2.4). We collected samples on three occasions (July 2014, March/ April 2015 and August 2015). During the first sampling round, all Dyke sites were still afforested, as restoration here began in October 2014. In March/ April 2015 only two of the three blocks were felled. For the purpose of this analysis we only included post-felling samples.
Figure 6.1: Chronosequence forest-to-bog restoration sites selected for pore and surface water quality monitoring. Blue plots are forest-to-bog restoration areas, within which orange plots are sampling sites. In Dyke, (felled 2014/15) each orange plot contained one sampling transect, while in the other restoration areas, each orange plot contained the three sampling transects for that site. Yellow plots are afforested controls and grey plots are open bog controls. Chronosequence sampling (3 rounds) was on July 2014, March/ April 2015 and August 2015.

Table 6.1: Chronosequence restoration sites and control plot characteristics

<table>
<thead>
<tr>
<th>Site name</th>
<th>Restoration year</th>
<th>Restoration age (years)</th>
<th>coded</th>
<th>Felling method</th>
<th>Drain blocks</th>
<th>Slope (degrees)</th>
<th>replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Talaheel</td>
<td>1997/98</td>
<td>17-18</td>
<td>R-17</td>
<td>fell-to-waste</td>
<td>n</td>
<td>2.1</td>
<td>3</td>
</tr>
<tr>
<td>Lonielist</td>
<td>2003/04</td>
<td>11-12</td>
<td>R-11</td>
<td>fell-to-waste</td>
<td>y</td>
<td>1.5</td>
<td>3</td>
</tr>
<tr>
<td>Raphan</td>
<td>2011/12</td>
<td>3-4</td>
<td>R-3</td>
<td>fell-to-waste</td>
<td>y</td>
<td>1.9</td>
<td>3</td>
</tr>
<tr>
<td>Dyke</td>
<td>2014/15</td>
<td>0-1</td>
<td>R-0</td>
<td>Standard felling: stem harvest, brash left on-site</td>
<td>y</td>
<td>1.9</td>
<td>6</td>
</tr>
<tr>
<td>Afforested controls</td>
<td>-</td>
<td>-</td>
<td>FOR</td>
<td>-</td>
<td>-</td>
<td>2.1</td>
<td>3</td>
</tr>
<tr>
<td>Bog controls</td>
<td>-</td>
<td>-</td>
<td>BOG</td>
<td>-</td>
<td>-</td>
<td>2.4</td>
<td>3</td>
</tr>
</tbody>
</table>

6.2.3 Sample preparation and analysis

Samples were refrigerated at 4°C on return to the laboratory and filtered, usually within 24 hours of collection (always within 36 hours) as described in Chapter 2.5. They were then analysed for concentrations of DOC, NH₄⁺, NO₃⁻, soluble reactive phosphate (SRP), S and a suite of macro (Ca, K, Mg, Na, S) and trace elements (Al, Cu, Fe, Mn, Ni, Zn; Chapter 2.5). DOC quality was also measured by absorbance (Chapter 2.5).

6.2.4 Statistical analyses

All the statistical analyses were performed using RStudio (Version 0.98.501, R Core Team, 2016). Samples from each plot were assigned to a class of open bog (BOG), afforested (FOR) or restoration age (Restoration 2014/15 (R-0), Restoration 2011/12 (R-3), Restoration 2003/04 (R-11), Restoration 1997/98 (R-17)) for statistical analysis. To look at the changes in water chemistry of the plot classes over time (represented by the chronosequence), we used principal response curves (PRC; package vegan, Oksanen et al., 2016), which allowed all classes to be compared to a chosen reference (van den Brink and Ter Braak, 1998, 1999), in this case the BOG plots. This multivariate method specifically tests the time by treatment interaction for a response matrix (log₁₀(x+1))
transformed water chemistry), enabling the visualisation of temporal trends in a given class in relation to the reference set *a priori* (Andersen et al., 2010). Temporal trends (through the chronosequence) were visualised as deviations from the reference rather than absolute values, with each class represented by a response curve. In addition, as this method is based on a redundancy analysis (RDA), it displays the strength of the different individual water chemistry variables with these temporal trends (van den Brink and Ter Braak, 1998, 1999). The significance of the principal response curves was tested using Monte Carlo permutations (n=999).

For WTD univariate statistical analysis was carried out at the class level to determine the effect of forest-to-bog restoration, between the restoration sites and FOR and BOG controls. A generalised linear mixed model was used (function *glmer*, package *lme4*, Bates et al., 2015), with “class” as the fixed factor. To account for repeated measures over time, “sampling round number” was added as a random effect (compound symmetry) as sampling rounds were either in 1. summer 2014, 2. spring 2015 or 3. summer 2015. “Plot” was added as a random intercept, to account for differences between plots within a class. Appropriateness of model fit was checked visually by normality of residuals and homoscedasticity of residuals (Crawley, 2007; Zuur et al., 2011). As the model had a statistically significant (*p*<0.05) effect of class, *a posteriori* Tukey adjusted pairwise comparisons were carried out (function *lsmeans*, package *lsmeans*, Lenth, 2016). Univariate statistical analysis were not carried out on the individual water chemistry variables to avoid the issue of multiple testing and a type I error occurring (Streiner and Norman, 2011), but also because we only had a small number of replicates. Instead, we focussed on graphical interpretation of trends with restoration over time and grouped variables according to their response to restoration.

Additionally, Spearman’s rank correlations were performed on all water quality variables to look at inter-relationships (function *corrplot*, package *corrplot*, Wei and Simko, 2016), showing both strength of relationships, Spearman’s Rho (Rₛ) and significance at the 95% confidence level. Spearman’s rank correlation was chosen as many of the variables were not normally distributed and as it does not assume linear relationships (Thomas et al., 2013).
6.3 Results

6.3.1 Trends in water chemistry across the chronosequence of forest-to-bog restoration sites

Water chemistry in forest-to-bog restoration sites (REST), varied significantly with time since restoration compared to the open bog reference sites (BOG) for surface water ($F=81.6$, $p=0.001$; Figure 6.2a), shallow pore water ($F=59.6$, $p=0.001$; Figure 6.2b) and deep pore water ($F=42.3$, $p=0.001$; Figure 6.2c). Water from afforested (FOR) was also clearly different to BOG sites. Surface and shallow pore water results implied a divergence from BOG (and FOR) conditions initially, with subsequent development towards BOG conditions. Deep pore water results suggest a gradual development towards BOG conditions throughout restoration. Overall restoration progress, measured as the position of restoration sites on PRC axes between FOR and BOG conditions, was nearly complete for deep pore water in 17 year old sites (R-17). At the same time point, restoration was about three-quarters complete for surface water, but only about 10% complete for shallow pore water.

In surface water, the REST curve showed a peak in concentrations of surface water chemistry variables (particularly DOC), which increased immediately following restoration (R-0) to levels higher than in FOR (Figure 6.2a). Three years later (R-3) concentrations decreased to levels below that of FOR sites. The downward trend in RES samples then continued to decrease more gradually, until the oldest restored sites (R-17), which were closest but still not aligned with the BOG reference. By 11-12 years following restoration (R-11), surface water chemistry was more similar to open bog control sites than FOR sites. The second noticeable pattern was the difference in the surface water chemistry between BOG and FOR sites. The variables most strongly associated with these trends were DOC, conductivity, Na, Mg and S, though we cannot separate out which were associated with FOR or REST sites here. (Figure 6.2a).

In shallow pore water, there was a large difference in water chemistry immediately following restoration (R-0), associated with more than two fold increases in DOC, phosphate and conductivity. The trend changed direction with time and the overall chemistry became more similar to FOR than to BOG sites 11-12 years after restoration (R-11). Shallow pore water chemistry continued to approach BOG but was still closer to FOR sites in the oldest restored sites. Ca and $NH_4^+$ also followed this overall trend, with
an initial rise in concentrations after restoration followed by a slow decrease after approximately three years (Figure 6.2b).
Figure 6.2: Principal Response Curves (PRC) for water chemistry for (a) surface water, (b) shallow pore water and (c) deep pore water using a space-for-time substitution, showing the first RDA axis, explaining the highest proportion of variation in the data. The left side of each panel represents overall deviation of forest-to-bog restoration sites of different ages (REST), from the open bog control sites (BOG), used as the reference state, along with the deviation afforested control sites (FOR) from the BOG reference. These are expressed as canonical coefficients on the first principal component axis (PC1), in comparison with the reference BOG sites which is represented by the zero line. The right hand side of each panel shows canonical coefficients for all the elements interpreted. A more positive coefficient shows a stronger relationship with the curve while a more negative coefficient suggests the opposite trend to the curve. The water chemistry parameters most strongly associated with the curves are therefore those, with the highest and lowest coefficients (green shading). 0.5 was used as the threshold to denote the main water chemistry parameters driving the trend (green broken line and arrow), with parameters scoring >0.5 or <-0.5 assumed to be the principal changes in water chemistry. Thus canonical coefficients represent variables driving deviation in both the REST and FOR treatments. The graph represents the period 0-1 year following restoration (2014/15) to 17-18 years following restoration (1997/98). To produce this analysis, it was assumed that the BOG and FOR sites remain constant over time, as can be the case in space-for-time substitutions. However, both BOG and FOR curves are constructed from samples from separate sites (n=3), on three separate sampling occasions. Phosphate is abbreviated to Phos, conductivity to Cond, temperature to Temp.

In deep pore water samples, the chemistry in REST was initially closer to FOR than BOG in the most recent restoration sites but the difference to BOG decreased over time (across the chronosequence). The variables that followed this trend more strongly included NH$_4^+$, Fe, Mg, S, Ca, conductivity and Na, while DIC appeared to show the opposite trend.

The second axis of the PRC showed background trends in water chemistry in FOR and REST relative to the BOG over time, representing 9.1 % (F=20.11, p=0.001) and 10.6 % (F=22.98, p=0.001) of total variation on the data, in surface and shallow pore water respectively. This axis suggests that in surface water DOC, phosphate and K were higher than both FOR and BOG immediately following restoration (R-0) and three years later (R-3). These then decreased through time approaching similar levels to BOG in the oldest restoration site (R-17). Additionally, this axis shows that conductivity, S and Na were consistently higher in FOR sites than BOG (Figure 6.3a).
For shallow pore water, the second PRC axis showed that DOC, temperature and the E4:E6 ratio were higher in REST than in BOG three years post-restoration (R-3) and did not recover with time. Again, the second axis suggests that conductivity and Na were consistently higher in FOR than BOG sites (Figure 6.3b). We did not present the second axis for deep pore water, as it only explained 3.0% of the variation in chemistry.

Figure 6.3: Second axis of Principal Response Curves for water chemistry for (a) surface water, (b) shallow pore water using a space-for-time substitution, showing the second RDA axis, explaining a lesser proportion of variation in the data. For details on interpretation of the y-axes see Figure 6.2.
6.3.2 Effects of forest-to-bog restoration on hydrology and water chemistry

6.3.2.1 Hydrological effects

Forest-to-bog restoration resulted in an increase in water table depth (WTD) over time, with the most recent restoration sites closer to that of FOR controls and the oldest restoration sites most similar to BOG (Figure 6.4). There was a significant treatment effect on WTD (X=29.31, p<0.0001); the R11, R17 and BOG sites were (22, 26 and 34 cm) significantly higher than FOR sites respectively, although WTD at R11 and R17 sites remained (on average) 12 and 8 cm lower than BOG controls.

Figure 6.4: Water table depth (WTD) in each of the forest-to-bog restoration ages and in open bog (BOG) and afforested control (FOR) plots. Boxplots show median and interquartile range with means (●). Treatments with the same letters were not significantly different. The x-axis labels show each site class. Restoration sites use the prefix “R” followed by age in years at time of sampling.
6.3.2.2 *Water chemistry variables showing a “legacy effect”*

In pore and surface water, both pH and Ca exhibited marked differences between FOR and BOG sites, with a trend for values in REST sites to move towards open bog conditions with time since restoration (Figure 6.4). However, recovery to BOG was either incomplete or only reached by the oldest restoration sites. This trend was termed a “legacy effect”.

The values for pH showed a similar trend to WTD, with lowest values in FOR and highest in BOG. In surface water, there was general pH increase with time since restoration, while in shallow and deep porewater high pH was also found in the 11 year old restoration site (R-11). For Ca, only the R-17 site had similar concentrations to open bog. In shallow porewater, Ca increased slightly following restoration (R-0), while in surface and deep porewater Ca concentrations decreased from FOR, through the restoration sites to BOG. In deep porewater Al and NH$_4^+$ exhibited similar patterns, with higher concentrations in FOR sites and in recently restored sites than in BOG. For Al, concentration appeared to have recovered by 11 years post restoration. NH$_4^+$ showed much greater amplitudes in the range of changes in concentration with a decrease through time, although not enough to reach concentrations as low as those found in BOG.
Figure 6.5: Response of water chemistry variables to forest-to-bog restoration which show a legacy effect of drainage and afforestation: defined by 1) a marked difference between FOR and BOG controls and 2) restoration sites over time moving from conditions similar to FOR to become more similar to BOG and 3) across the restoration sites recovery to BOG conditions is not achieved or only in the oldest restoration site (17 years; R-17). (a) pH in surface water (b) pH in shallow porewater, (c) pH in deep porewater, (d) Al in deep porewater, (e) Ca in surface water (f) Ca in shallow porewater (g) Ca in deep porewater (h)
\( \text{NH}_4^+ \) in deep porewater, in each of the forest-to-bog restoration ages (denoted R-age) and in open bog (BOG) and afforested control (FOR) plots. Boxplots show median and interquartile range with means (●).

### 6.3.2.3 Water chemistry variables showing an effect of restoration

Effects of restoration were defined as a marked change (increase or decrease) in water chemistry variables following restoration where the difference between BOG and FOR was otherwise comparatively small. Graphically, this was visible as a “bell” (or inverted bell) shape. This trend was exhibited by DOC, colour to carbon ratio, E4:E6 ratio, \( \text{NH}_4^+ \), phosphate, K, temperature, Zn, Al and Fe (Figure 6.6, 6.7). In most cases, they displayed an increase in concentrations immediately following or three years after restoration and were largely limited to surface and shallow pore water.

Immediately following restoration, DOC concentrations in surface and shallow pore water increased to a mean of \( \geq 100 \text{ mg L}^{-1} \), from \( < 50 \text{ mg L}^{-1} \) in FOR sites (Figure 6.6a-b). DOC concentrations decreased with time since restoration recovering to levels similar to FOR, 17 years post-restoration but remained higher than BOG. The colour to carbon ratio in surface water showed an increase with time since restoration to levels higher than BOG, while in shallow porewater it initially decreased and then recovered towards BOG (Figure 6.6c-d). The E4:E6 ratio in surface water following restoration was similar to BOG and FOR (0-3 years). By 11 years post-restoration it increased (factor of 1.5) and began to recover in the oldest restoration site (Figure 6.7e).

Phosphate and K exhibited a similar trend post-restoration in surface and shallow porewater (Figure 6.6g-j). Sharp increases were implied by the respective 40-330-fold and 5-fold higher values in early restoration sites (R-0). Concentrations remained high three years post-restoration but recovered to FOR and BOG levels by 11 years after restoration. The concentrations of phosphate or K did not appear different between BOG and FOR controls. In contrast, \( \text{NH}_4^+ \) increased slightly immediately following restoration in shallow pore water but by three years post-restoration concentrations tripled compared to that of FOR (Figure 6.6f). \( \text{NH}_4^+ \) continued to decrease with time following restoration but did not recover to match BOG sites.
Figure 6.6: Response of water chemistry variables to forest-to-bog restoration which show a restoration effect: defined by 1) a bell shaped curve from the restoration sites to indicate an increase or decrease in concentrations out with the range of FOR and BOG controls. (a-b) DOC, (c-d) colour to carbon ratio (254nm), (e) E4:E6 ratio, (f) NH4+ (g-h) phosphate, (i-j) K, (k-l) temperature in surface water and shallow porewater, across each of the forest-to-bog restoration ages (denoted R-age) and in open bog (BOG) and afforested control (FOR) plots. Boxplots show median and interquartile range with means (●).
Temperature in surface water and shallow porewater increased following restoration until 11 years post and then decreased towards BOG (Figure 6.6k-l). BOG sites were higher than FOR. This trend was also present in deep pore water (data not shown).

Zn exhibited an effect of restoration in surface, shallow and deep pore water, with highest mean concentrations either three years post-restoration (shallow pore), 11 years post-restoration (surface) or 17 years post-restoration (deep; Figure 6.7a-c). Compared to FOR sites, peak mean concentrations were up to 11-fold higher. FOR and BOG had similar Zn concentrations and the oldest restoration site seemed to remain higher than both at all depths.

Al concentrations increased immediately post-restoration in surface and shallow pore water and did not recover to concentrations similar to BOG until 17 years post-restoration (Figure 6.7d-e). However, in this case FOR sites were higher than BOG, showing in part also a legacy effect of forestry in restoration sites. Similarly, Fe concentrations in shallow porewater increased following restoration but three years afterwards, had decreased to levels lower than FOR (Figure 6.7f). Concentrations continued to decrease over time.
Figure 6.7: Response of water chemistry variables to forest-to-bog restoration which show a restoration effect: defined by 1) a bell shaped curve from the restoration sites to indicate an increase or decrease in concentrations out with the range of FOR and BOG controls. (a) Zn in surface water, (b) Zn in shallow porewater, (c) Zn in deep porewater, (d) Al in surface water (e) Al in shallow porewater and (f) Fe in shallow porewater, across each of the forest-to-bog restoration ages (denoted R-age) and in open bog (BOG) and afforested control (FOR) plots. Boxplots show median and interquartile range with means (●).
6.3.2.4 Water chemistry variables mostly influenced by conifers – “forestry effects”

Mg, Na, S, conductivity and Fe were highest in FOR sites. Shortly after restoration (R-0) years, levels were similar to FOR sites. In many cases (particularly in surface water), recovery to concentrations similar to BOG was shown by three years post-restoration. However, by 11 years post-restoration all were more similar to BOG than FOR (Figure 6.8). Thus, these variables exhibited a short-medium term influence of the forestry. These effects were present at all depths (surface and pore water), except for shallow pore water Fe (effect of restoration). Mg, Na and S showed a very similar trend of recovery from forestry with restoration over time, however concentrations of Na were around a factor of 10 greater than Mg or S. The trend in surface water Fe was very subtle (Figure 6.8d) and in deep porewater Fe (Figure 6.8k), the most marked difference was between FOR and R-0 sites where mean concentrations decreased by ~75%.
Figure 6.8: Response of water chemistry variables to forest-to-bog restoration which show a forestry effect: defined by 1) a marked difference between FOR and BOG controls and 2) restoration sites moving from conditions similar to FOR towards BOG by 3-11 years and complete recovery is achieved. (a-c) Mg in surface water, shallow and deep pore water respectively, (d) Fe in surface water, (e-g) Na in surface water, shallow and deep pore water respectively, (h-j) S in surface water, shallow and deep pore water respectively, (k) Fe in deep pore water (l-n) conductivity in surface water, shallow and deep pore water respectively, in each of the forest-to-bog restoration ages (denoted R-age) and in open bog (BOG) and afforested control (FOR) plots. Boxplots show median and interquartile range with means (●).
6.3.2.5 Correlations in water chemistry variables

There were strong (>0.6) positive correlations between Ca, Mg, Na and conductivity at all depths (Figure 6.9). In shallow pore water, this group of correlated variables also included S and strong negative correlations (< -0.6) with pH, while in surface water all of the above correlations were found and Al was strongly positively correlated with most of these elements.

In surface water there were also strong positive correlations between Al, Fe, DOC and phosphate, while in shallow pore water only DOC and phosphate were strongly correlated. In shallow and deep pore water TON concentrations exhibited a strong negative correlation with pore water temperature. In surface water and shallow pore was a weaker positive correlation between DOC and temperature ($r_s = 0.52$ and 0.54 repetitively). The number of significant strong correlations decreased in the order surface water > shallow pore water > deep pore water.
Figure 6.9: Spearman’s rank correlation coefficients for (a) surface water, (b) shallow pore water and (c) deep pore water chemistry, analysed as all variables measured dataset (Cu, Ni, colour to carbon measures at 400 and 254nm were excluded). Correlations significant at the 95% confidence level (p < 0.05) are shaded according to the strength of the correlation.
6.4 Discussion
There were clear differences in the water chemistry of afforested (FOR) and open bog (BOG) sites in surface and both shallow and deep pore water (Figures 6.2, 6.3), which confirms that water chemistry could be a useful measure of recovery in forest-to-bog restoration sites. In general, we found three trends in water chemistry (across the chronosequence) with variables showing: 1) legacy effects, i.e. moving from FOR to BOG recovering only by 17 years post-restoration or not recovering completely; 2) restoration effects i.e. marked changes in concentrations above that of both FOR and BOG controls exhibited in the restoration sites within 3 years of management, 3) forestry effects, i.e. rapid recovery (3 - 11 years), in surface and pore water following tree removal.

Similar patterns in water chemistry with time since restoration were also shown by the multivariate (PRC) relative to BOG controls. The deep pore water curves moved from being similar to FOR conditions, with recovery almost to BOG conditions within 11 years captured by the chronosequence (effect of forestry). On the other hand, the shallow pore water curves had an initial peak, representing the “bell shape” effect of restoration as a disturbance to water chemistry. Although this effect decreased with time since restoration, shallow pore water chemistry did not recover to BOG conditions within the 17-18 years since restoration suggesting some legacy effects too. This is in agreement with the patterns in pore water chemistry between pristine and 10-year-old restoration sites in Finland, some of which were previously drained to increase natural forest cover (Haapalehto et al., 2014).

In surface water there was first a disturbance-related increase in concentrations of DOC in particular (effect of restoration), which began to decrease over time. This is similar to observations by Muller and Tankéré-Muller (2012) in the same area. In the R-3 site, surface water chemistry already began to recover towards BOG and by 17-18 years post-restoration was closer to BOG than FOR (~75% recovered), thus integrating both legacy effects and forestry effects. The high axis scores for Na, conductivity, Mg and S were due to the marked differences between FOR and BOG sites, and the recovery in restoration sites over time.

6.4.1 Hydrology and chemistry feedbacks
One of the major influences on peatland pore and surface water chemistry in restored sites is WTD (Andersen et al., 2010). For example, the change in redox conditions as WTD
increases, would be expected to result in reduction of S, Fe and N compounds, changing their soluble concentrations in porewater (Bowden, 1987; Steinmann and Shotyk, 1997; Mandernack et al., 2000). Thus we would expect lower TON than NH$_4^+$ in porewater (we observed TON concentrations 10-20 fold lower), due to anoxic conditions, preventing nitrification of organic N through to nitrite and nitrate (Bowden, 1987; Megmw and Knowles, 1987). TON did not show any trend across our sites (data not shown), although generally, nitrifying bacteria are more associated with water table drawdown, thus higher TON may be expected where WTD is lower (FOR and R-0; Andersen et al., 2013b).

The step increase in WTD following restoration showed recovery over time and the clear differences between FOR and BOG land uses. A similar pattern of WTD recovery since forest-to-bog restoration was observed in Finnish peatlands, one, two, three and 10 years post-restoration, however the difference between three and 10 years post-restoration was no greater than annual differences in the first three years (Haapalehto et al., 2011). Similarly, in our study the largest increase in mean WTD was between the FOR and most recent restoration site (R-0). As the oldest restoration site did not have as high WTD as BOG this suggests a legacy effect of drainage and afforestation on WTD and that more time was required to reach the level of open bog or further management intervention. However, a recent study of vegetation recovery on the R-17 site, showed that moisture conditions as indicated by plants had overall recovered, although further re-wetting may help recovery of other restoration outcomes (Hancock et al., in prep.). We acknowledge that our WTD measurements were spatially limited to our sampling locations and did not cover the entire restoration area.

### 6.4.2 Water chemistry variables showing a legacy effect

The increase in pH in restoration sites shows a slow but incomplete recovery from the legacy of the acidifying effect of forestry. Forestry can acidify soils through a number of mechanisms. First, acidification can be partly due to scavenging of atmospheric S and N (Fowler et al., 1989; Nisbet and Evans, 2014). Additionally, forests enhance sea salt deposition i.e. marine sourced Na and Mg, which through cation exchange displace acid cations in soil (H$^+$, Al$^{3+}$), thus contributing to the acidity of pore and surface water (Neal et al., 1986; Evans et al., 2001).
Another contributor of acidification in forest soils is base cation depletion from uptake by growing trees (Nisbet and Evans, 2014), although in our study Ca, Mg and K were highest in the FOR sites and declined with time since restoration so was not likely to be a cause here.

One possible explanation for higher Ca in FOR sites may be that deeper tree roots enhance weathering in the mineral later beneath shallow peats, where nutrients e.g. Ca and Mg are available (Vejre and Hoppe, 1998). There may also be some Ca inputs from wet deposition (Proctor, 2006), intercepted by the tree canopy which may additionally contribute Ca to throughfall (Schmitt and Stille, 2005). Therefore, following restoration, these sources of Ca disappeared and Ca concentrations could have started to decrease. However, we observed a slight increase in shallow pore water Ca immediately following restoration (R-0) first, which may have been related to re-working of the surface by machinery, causing some mineral input through disturbance.

The highest NH₄⁺ concentrations in this study were generally in deep porewater in FOR sites. Following planting, exudation by active conifer roots (Wieder et al., 1985) and mineralisation of organic N during periods of WTD drawdown (Daniels et al., 2012) could have both contributed to increasing the NH₄⁺ pools. In all the restoration sites, NH₄⁺ concentrations remained higher than BOG possibly through release from decomposed peat through re-wetting (Zak and Gelbrecht, 2007).

### 6.4.3 Water chemistry variables showing a restoration effect

Following forest-to-bog restoration, DOC concentrations in surface and shallow pore water increased immediately which concurs with results from other re-wetted or restored peatlands (Fenner et al., 2001; Chow et al., 2003; Clark et al., 2012). The main mechanism explaining this phenomenon is likely the stimulated enzyme activity that is commonly observed in drought-rewetting cycles (Fenner et al., 2011; see chapter 3.4). In the first year following restoration (R-0 site), brash decomposition would likely contribute (most) to DOC concentrations in pore and surface water (Hyvonen et al., 2000; Palviainen et al., 2004a).

In the longer-term, DOC concentrations in restoration sites have been observed to decrease below those of equivalent unrestored drained sites (Wallage et al., 2006; Höll et al., 2009) or afforested sites (Haapalehto et al., 2014). This contrasts with our restoration
sites, where, DOC decreased over time in restoration sites towards BOG, but remained ~2 fold higher 17 years post-restoration. A major influence on the decreasing DOC concentrations over time may be the relative (between-season) stabilisation of WTD (Höll et al., 2009; Andersen et al., 2010), compared to the rapid (19cm) WTD rise in the first year following restoration. As no restoration sites reached mean DOC concentrations as low as BOG, this suggests continued enhanced microbial activity in REST compared to BOG (Bardgett et al., 2008).

Another potential indicator of microbial activity (decomposition) is the colour to carbon ratio, where a higher ratio can suggest enhanced microbial activity (Wallage et al., 2006). However, in surface and shallow pore water, the colour to carbon ratio was highest in the oldest restoration and BOG sites respectively, where the lower DOC concentrations already suggested lesser decomposition than in other sites.

We also studied DOC quality using the E4:E6 ratio. In surface water, this suggest that mostly young carbon was being lost in runoff from all sites, being closer in nature to fulvic acids than humic acids (Wallage et al., 2006). However, surface water is also diluted by precipitation (Proctor, 2006) and both shallow and deep pore water had lower ratios suggesting some influence of humic acids (data not shown). We observed a slight increase in the E4:E6 ratio with time since restoration in surface and shallow pore water, potentially indicating that the proportion of more decomposed (older) humified matter in DOC was decreasing, as found by Wilson et al. (2011) in restored open blanket bog. Our results show this was also evident to a lesser degree in deep pore water.

The peak in Fe and Al in shallow porewater immediately following restoration (R-0 sites) was similar to that exhibited by DOC and may be a consequence of the associations often found between DOC and Fe (Krachler et al., 2010) and Al (McKnight and Bencala, 1990), and is also supported by their positive correlations with each other. For Al, this may be related to release from decomposition from needles in the early restoration years (Asam et al., 2014a) but may also be associated with surface disturbances which affect the mineral layer (Chapter 3.4.2). There was also signs of legacy effects on Al concentrations from FOR sites, which may be a long lasting effect of disturbance through ploughing (Muller and Tankéré-Muller, 2012) or displacement of Al from cation exchange sites by scavenged cations from conifers (Evans et al., 2001).
In shallow and surface pore water, the elevated (> factor 40) phosphate and (> factor 5) K concentrations in the year following restoration (R-0), likely resulted from needle and brash decomposition respectively (Palviainen et al., 2004; Kaila et al., 2012; Asam et al., 2014; see chapter 3.4.1). However, concentrations of both phosphate and K decreased in the R-3 site and continued to decrease to the levels of BOG sites, 11-12 years post-restoration (R-11 site), showing complete recovery.

In shallow pore water, maximum $\text{NH}_4^+$ concentrations were measured in the R-2011/12 site (3-4 years post-restoration), suggesting a slower release of N compared to P and K. This agrees with rapid release of P relative to N experimentally demonstrated from forest litter (Moore et al., 2011). Even 17-18 years after restoration, $\text{NH}_4^+$ concentrations in shallow pore water were still 11-fold higher than bog (7.5 fold in R-11); therefore, under the current management, more time appears to be required for recovery in N.

The trends in surface and pore water temperature was likely related to shading by trees in FOR sites (lowest temperatures) and a lack of shade in restoration sites, as found by Ormerod et al. (1987) in afforested streams. The lower temperatures in the oldest restoration (R-17) and BOG sites may have been due to a higher albedo effect, due to increased Sphagnum cover (Berglund and Mace, 1972; Tsuyuzaki et al., 2009). Higher temperatures in the newest and medium aged restoration sites (R-0, R-3, R-11) may stimulate decomposition in these sites (Davidson and Janssens, 2006).

Interesting trends in Zn were found with time, with greater concentrations found in older restoration sites than either FOR or BOG. As Zn is normally present in micronutrient levels in trees, mainly from atmospheric sources (Boardman and McGuire, 1990), some release may be expected during decomposition of brash and needles. Other studies have found both Zn accumulation and release from conifer needles (Asam et al., 2014a) and increased concentrations in surface water following clear felling (Kiikkilä et al., 2014), but it is the first time (to our knowledge) that the length of this effect is documented in peatlands undergoing restoration.

6.4.4 Water chemistry variables showing a forestry effect

Concentrations of Mg, Na, S were highest in FOR sites and decreased through time. For all three elements, concentrations recovered to similar concentrations to BOG within a decade post-restoration, showing that they were more strongly influenced by the presence
of the trees themselves rather than by legacy effects from the forestry. Indeed, concentrations of all three elements are enhanced by forest capture (Harriman and Morrison, 1982; Evans et al., 2001) and a similar trend in recovery of Na in (former peat forest) restoration sites, towards bog levels was found by Haapalehto et al. (2014). Mg and Na are generally from marine sources, while S can be both industrial and marine (Harriman et al., 1995, 2001).

In in FOR sites, high S concentrations could be due both to scavenging S by conifers (Nisbet and Evans, 2014) and to hydrological feedbacks (Clark et al., 2005). Where WTD is lower, sulphate is produced by the oxidation of reduced inorganic/ organic sulphur (Adamson et al., 2001; Chapman et al., 2005), contributing to the higher concentrations of S in porewater in FOR and recent restoration sites. Conversely, when the WTD rises, anaerobic bacteria reduce sulphate back to less soluble states (hydrogen sulphide, reduced inorganic sulphur, organic bound sulphur; (Mandernack et al., 2000; Adamson et al., 2001), which helps explain the concentrations decrease we observed.

The trend in conductivity with restoration followed that of two base cations (Mg, Na) and was generally highest in FOR sites. It did not reflect the legacy effect on Ca, despite being a summative measure of ions (Vogt et al., 2010).

6.4.5 Implications for restoration success
In terms of the progress on recovery to bog, some individual water chemistry variables showing an effect of restoration recovered to levels similar to BOG 17-18 years post-restoration (phosphate and K), while others did not (NH$_4^+$). The elevated NH$_4^+$ in shallow pore water, suggests a difference in mineralisation rates been R-17 and BOG sites (Andersen et al., 2013b), likely caused by the continued decomposition of brash and tree material. Along with poor retention of P by peat (Rodgers et al., 2010; Asam et al., 2012b), the continued release of N can result in an imbalance of N and P, which is thought to hamper recovery (Andersen et al., 2010).

Increased levels of N can increase bacterial biomass but cause microbial P limitation, stimulating N release and P retention by microbes (Bragazza et al., 2012a). This in turn encourages vascular plant growth, while discouraging Sphagnum (Xing et al., 2011). The remaining NH$_4^+$ in shallow porewater may be in part responsible for the variable response in Sphagnum spp. at the oldest restoration site (R-17; Hancock et al., in prep). However,
in order for successful restoration to occur both good *Sphagnum* cover and a seasonally stable water table are required (Andersen et al., 2010) and as yet, WTD has not completely recovered.

In the shorter term following restoration (R-3), there were elevated concentrations of phosphate and K, when NH$_4^+$ began to increase. An excess of N, P and K together has been found to have a stronger positive effect on vascular plants and negative effect on *Sphagnum* mosses, than N alone (Bubier et al., 2007; Larmola et al., 2013). This suggests the starting point of forest-to-bog restoration sites may also be less conducive to recovery of bog vegetation and that removing the source of excess nutrients (conifer stems plus brash) may help this initial recovery. However, in the first year following restoration, stem plus brash harvest was found to cause greater nutrient release than stem only harvest, possibly by increased surface disturbance (Chapter 3).

The legacy effect of Ca concentrations may also present a barrier to *Sphagnum* colonisation in the first decade post-restoration, when concentrations were elevated above BOG sites. *Sphagnum* sp. are known to have different niche overlaps in terms of Ca tolerance (Bragazza, 1997) but in general growth can be impaired under elevated Ca concentrations (Gorham and Pearsall, 1956; Spatt and Miller, 1981). However, this effect is strongest when pH is also elevated (Clymo, 1973) and therefore referred to in characterising bogs, as peatlands where pH ranges from 3.8-4.25 and Ca concentrations is <2.1 mg l$^1$ (Glaser et al., 1981; Gorham and Janssens, 1992).

As acidification of surface waters is one of the principle impacts of afforestation on water quality (Nisbet, 2001; Nisbet and Evans, 2014), pH is therefore a key recovery indicator in the restoration of afforested peatlands. The legacy effect observed here, showed that pH in pore- and surface-waters remained lower than open bog, therefore the scavenged elements and displaced acid anions were not completely diluted, 17 years post-restoration. The key concern with pH is its importance for recovery of stream ecology e.g. low pH can negatively affect salmon numbers in afforested streams (Harrison et al., 2014) and increase the ecotoxicity of dissolved Al (Kroglund et al., 1999). However, despite the acidification of pore- and surface water and some acidified first order streams, we did not detect deleterious effects on the pH of major rivers in this study (Chapter 4).

The current restoration method of fell-to-waste and drain blocking was effective in initiating recovery, though it would appear that more than 20 years are required to align
with BOG pore and surface water chemistry, if at all. When considering all water chemistry variables together, greatest recovery towards open bog conditions was achieved in surface water and deep pore water, with lesser recovery in shallow pore water. This suggests that shallow porewater was most disturbed by restoration through a combination of the following factors: 1) water table fluctuation, 2) physical disturbance from machinery and 3) vertical leaching from decomposing brash. Therefore, future management techniques should address these current barriers to enhance recovery. Some of the most recent forest-to-bog restoration methods seek to do this (Chapter 6.4.6).

A level of caution should be applied to these findings as trees on restoration sites were of different ages when felled, which may have shortened recovery time in older restoration sites. For example, the quantities of nutrients released by trees in the R-17 and R-11 sites may be less than if these sites had held mature stands, due to a greater quantity of biomass left on site (e.g. Saarsalmi et al., 2010). On the other hand, drains were not blocked on the oldest restoration site until after sampling was completed and WTD recovery relied on natural in-filling of the drains and furrows (Holden et al., 2007; Hancock et al., in prep.); and this may have delayed initial recovery. The other factor is that the most-recent restoration sites may be more disturbed due to a longer period under drainage and forestry, leading to greater loss of bog vegetation and greater decomposition of peat (Laine et al., 1995). In any case, this highlights further the need to continue some level of long-term monitoring to understand whether recovery time can be reduced by management.

6.4.6 Implications for management
Current forest-to-bog management practice uses harvesting rather than fell-to-waste as trees are larger and income from timber can help offset some of the costs of restoration (Anderson, 2010). Additionally, this removes much of the decomposable tree material, which contains nutrients (Anderson et al., 2016), which can be released over time (Moore et al., 2011). More enhancements to forest-to-bog restoration are now being trialled (furrow blocking, brash crushing or harvesting, stump flipping) to assess the most effective method (Anderson and Peace, 2017; Hancock et al., in prep.; Andersen et al., 2016). Therefore, this research provides an insight into the restoration process of transforming plantation forestry back to open bog although future methods may be able to accelerate and enhance this recovery somewhat.
Our results show that the greatest barriers to recovery are a lower WTD and elevated N in the oldest restoration site (R-17), therefore removing the source of nutrients by harvesting brash and stems is, in theory, a good solution. In the short term, this may have been enhanced by the extra surface disturbance from brash harvesting machinery (Chapter 3), which is a caveat of enhanced harvesting methods. Longer term monitoring of this treatment would allow us to understand the dynamics of the initial nutrient pulse in surface and shallow pore water. Blocking of plough furrows can be undertaken to further raise the water table, which may be a more important factor than water chemistry to help Sphagnum recovery (Bragazza, 1997). In turn, reaching a high WT more rapidly, may feedback on water chemistry, and in particular processes that are influenced by redox-conditions.

The increased concentrations of pore and surface water chemistry variables, resulting from the initial disturbance of forest-to-bog, which lasted or peaked within 3-4 years post-restoration (R-3 site; DOC, phosphate, K and NH$_4^+$) indicate potential negative effects on stream water quality over a similar time period. However, as not all of these parameters significantly increased in streams in the first year post-restoration and did not affect Water Framework Directive or drinking water quality standards in rivers (Chapter 4), the risk of longer term effects appears low. This is assuming a similarly small percentage of the catchment area is undergoing restoration, which is an important influence on stream water quality (Nieminen, 2004; Palviainen et al., 2014).

Our results, show that surface and pore water quality are useful indicators of recovery in the restoration of afforested peatlands, especially when carried out across decadal timescale in comparison to control sites. It is important to monitor water chemistry variables which are both different in FOR and BOG sites, with a legacy of slow recovery e.g. pH, as well those which are not different in FOR and BOG sites but are affected by restoration. Monitoring of these water chemistry variables along with WTD (Figure 6.10), can provide key indications of nutrient cycling, and therefore influence vegetation recovery and progress towards open bog.
Figure 6.10: Surface and pore water quality variables which can be used as indicators of recovery in the restoration of afforested peatlands. These include variables which were found to show legacy effects of drainage and afforestation and variables which were directly affected by restoration. Our results suggest that along with WTD, recovery of these water chemistry variables (underlined) are key to achieving functional conditions similar to blanket bog. Al and Zn are included as elements with the potential to cause adverse impacts in downstream ecosystems, therefore monitoring of these is also recommended.

6.5 Conclusion
Currently our results suggest that more than 20 years is required for complete recovery of water chemistry to bog conditions and may help explain why some of the characteristic bog plants do not come back readily. However, newer restoration methods of conifer harvesting (stem plus brash) and blocking of plough furrows to increase the WTD, may be able to remove the main barriers to recovery (WTD and N levels) and accelerate the restoration process. In this way forest-to-bog restoration sites may be reach blanket bog functioning faster. We conclude that monitoring of surface water and pore water chemistry is useful in indicating recovery to bog and we recommend monitoring of WTD, pH, DOC, NH₄⁺, phosphate, K and Ca as key variables.
7. Discussion

This chapter will start with a summary of the main findings from each of the data chapters (3-6) and then consider “the effects of bog restoration in formerly afforested peatlands on water quality and aquatic carbon fluxes” across spatial and temporal scales, and the implications for management and for peatland function.

7.1 Chapter 3 – Pore and surface water quality in the first year following forest-to-bog restoration

In the first year following forest-to-bog restoration (0-1 year after), we found significant increases in concentrations of DOC, phosphate, K and NH$_4^+$ in surface water and shallow pore water relative to standing forest and open bog control plots. DOC concentrations increased 2-fold, NH$_4^+$ 4-15-fold, K increased 3-fold in shallow pore water and up to 11-fold in surface water, while phosphate increased up to 33-fold in shallow pore water and 99-fold in surface water. WTD increased significantly following restoration, relative to forest and bog controls, with a mean rise of 10.0 cm in restoration plots.

In general, there were some differences in the responses, depending on the restoration treatment. “Standard” fell plots (stem harvest, brash left on site in brash mats) had greater increases in water quality variables in shallow pore water, while “enhanced” fell plots (stem plus brash harvest) showed greater increases in surface water. Changes in concentration all showed a strong seasonal effect with increases from June 2015 and with DOC, phosphate and K declining slightly by December 2015. In deep pore water, there were fewer effects of restoration with smaller (<1.5 fold) but significant increases in DOC, Mg and conductivity occurring.

The increased concentrations of plant nutrients may have implications for colonisation by bog vegetation, as nutrient addition is known to decrease Sphagnum abundance and increase that of vascular plants (Bubier et al., 2007; Larmola et al., 2013). At present, after one year of post-restoration monitoring, we cannot determine the best restoration method, due to the differing responses in water chemistry of the “standard” and “enhanced” fell methods in surface- and shallow pore-water. The sharper and larger increases in DOC, plant nutrients and metals (Ca, Al, Fe) which occurred in surface water within the “enhanced” plots, declined by December 2015. This suggest “enhanced” felling may have a lesser impact on water chemistry over longer time periods, but it would
be necessary to determine whether similarly high peaks in surface water concentrations occur in subsequent summer seasons. Similarly, we suspect that the slower response in “standard fell” plots, may show continued increases in surface and pore water concentrations, as brash continues to slowly decompose, although this also may be influenced by seasonal patterns. We suggest that future monitoring of plant nutrients (NH$_4^+$, phosphate, K), DOC and WTD in surface and shallow pore water should be undertaken in the coming 2-5 years, along with surface vegetation, to assess recovery to bog conditions over this time period and guide future restoration management of afforested blanket bog.

7.2 Chapter 4 – Stream and river water quality in the first year following forest-to-bog restoration

We investigated the short term (0-1) year effects of forest-to-bog restoration on water quality in streams and rivers. Here, we found significant increases phosphate (4.4 fold) and Fe (1.5 fold) in streams draining restoration areas relative to forest and bog controls, but there were no significant concentration changes in rivers. We also observed (1.3-2 fold) increases in DOC and turbidity (not significant) and K and Mn (not statistically tested) in restoration streams. Increased Al concentrations in some restoration and afforested control streams (1.5 fold) were associated with forestry/ access track disturbances. All of these concentration increases included a seasonal element, peaking in summer 2015. We found no significant effect of restoration on pass rates against the Scottish Government applied EU WFD standards or UK drinking water standards, although we observed a greater number of occasions (25%), when phosphate did not reach the target “good” status in rivers.

These results were attributed to felling small percentages of the stream (3-23%) and river (≤ 3%) catchments and the use of drain blocking and silt traps. For future restoration, we recommend following these measures. We also suggest the harvesting of brash and needles, may help mitigate against effects on stream and river water quality, although we did not specifically test it here, as “standard” and “enhanced” felling were both carried out in each stream catchment. With continued forest-to-bog restoration in the same stream catchments within two to four years, the total felled area will increase with both the new and current restoration areas contributing to water quality changes. Therefore, a potential solution to mitigate against water quality deterioration may be to combine brash removal
with the use of buffer areas, to remove nutrients and SPM.

7.3 Chapter 5 – Aquatic carbon export in the first year following forest-to-bog restoration

We measured concentrations and exports of aquatic carbon species in a catchment undergoing forest-to-bog restoration, an open bog catchment and a catchment with predominantly plantation conifers in a before-after-control-impact (BACI) design. We found no significant increases in concentrations or export of aquatic carbon species (DOC, POC or DIC) in the first year following forest-to-bog restoration. However, restoration likely caused increased DOC concentrations in the first summer (2015) and there was some indication of changes in the patterns of DOC loss during storm events. The lack of significant immediate effects of forest-to-bog restoration may be a consequence of the small proportion of the catchment (12%) undergoing this management. Thus, if further restoration occurs within in future years (0-3), there may be additional effects on aquatic carbon. The harvesting of stems and brash may help to mitigate any further effects (by removing a DOC and POC source), along with the blocking of plough furrows to help retain water in the restoration area. However, the management objective (e.g. nature conservation, drinking water supply) will determine restoration aims and whether additional measures (e.g. brash removal) are required for key ecosystem services from the catchment.

In general, catchment characteristics and discharge (including the effect of storms), were important to aquatic carbon export. In the post-restoration year (2015), DOC export increased by 28% and 32% in the restoration and open bog catchments respectively. This may have been due to a large (40%) increase in mean discharge in the open bog catchment, related to a change in precipitation patterns, lower temperatures and higher water tables. Whereas, in the restoration catchment increased DOC export may have resulted from both increased DOC concentrations and discharge. Despite this, the restoration catchment actually showed lower increases in DOC export than intact bog, between the two years.

Additionally, there were seasonal differences in DOC concentration trends during storms, with generally increasing concentrations during summer and autumn storms, while in winter and spring concentrations decreased or remained constant. We found a similar response to storm events in the restoration, open bog and afforested catchments with larger storms causing a greater increase in export, across all three habitat types. These
seasonal effects and overall patterns were similar among the three habitat types, implying relatively little impact of forest-to-bog restoration on DOC export during the study period.

7.4 Chapter 6 – Measuring restoration progress using pore- and surface-water chemistry across a chronosequence of formerly afforested blanket bogs

In this chapter, we measured pore- and surface-water chemistry across a chronosequence of formerly afforested blanket bogs in comparison with standing forest and open bog controls. Our results imply progress in recovery towards open bog conditions during 0-17 years post-restoration. There were some legacy effects of drainage and afforestation, which recovered almost to open bog conditions (WTD, pH), while elements scavenged by trees (Mg, Na, S), completely recovered. Water chemistry variables which showed an effect of restoration recovered by ≤11 years, except NH$_4^+$, DOC and Zn which remained elevated compared to open bog 17 years post restoration. Excess N and lower WTD may have implications for the recovery of recovery of bog vegetation including key Sphagnum species.

Currently our results suggest that more than 20 years is required for complete recovery of water chemistry to bog conditions and may help explain why some of the characteristic bog plants do not come back readily. However, newer restoration methods of conifer harvesting (stem plus brash) and blocking of plough furrows to increase the WTD, may be able to remove the main barriers to recovery (WTD and N levels) and accelerate the restoration process. In this way forest-to-bog restoration sites may reach blanket bog functioning faster. We conclude that monitoring of surface water and pore water chemistry is useful in indicating recovery to bog and we recommend monitoring of WTD, pH, DOC, NH$_4^+$, phosphate, K and Ca as key variables.

7.5 Synthesis discussion: the effects of bog restoration in formerly afforested peatlands on water quality and aquatic carbon fluxes

The water quality parameters most affected by forest-to-bog restoration were DOC and plant nutrients (phosphate, NH$_4^+$ and K) along with Ca, Fe and Mn. These were associated with either WTD changes, decomposition of brash and needles or physical disturbances (Table 7.1). Here, we address the issue of scale and impacts i.e. were in situ changes in pore and surface water with implications for recovery to bog also detectable in streams.
draining restoration plots and major rivers (Dyke or Halladale), with implications for water quality of the downstream ecosystem?

In general, the largest effect sizes were in pore- and surface-water, for phosphate, NH$_4^+$ and K (Table 7.1). However, only phosphate also showed significant increases in streams and was the only variable to show signs of a small effect on rivers. Brash appeared to be associated with most concentration increases in pore- and surface- water (DOC and nutrients), while in streams the significant effects could be associated with brash, rising water tables and physical disturbance. Additionally, there are a number of specific mechanisms and feedbacks contributing to water quality and hydrology changes occurring in pore- and surface-water (Figure 7.1).

Table 7.1: Effect size of restoration on water chemistry parameters measured in shallow pore-water, surface-water and streams/rivers, 0-1 year post-restoration. The top section lists key parameters, where there were significant effects forest-to-bog restoration found. Effect sizes are the mean post-restoration concentrations divided by mean pre-restoration concentrations in restoration sites at each scale. The range given for pore- and surface-water refers to the range of effect sizes in standard fell (stem harvest only) and enhanced fell (stem and brash harvest) treatments. Grey shading indicates effects which were significant relative to standing forest and open bog controls. The association columns, indicate the main known cause of such effects; brash, water table (WT) or physical disturbance. As changes in Mg, Na, pH and conductivity were small (<1.5 fold), no associated causes are indicated.
Significant effects for Fe were found at the stream level, but were not statistically tested using univariate statistics in surface- or pore-water. This was due to the use of the threshold (>0.5 score) in the principal response curves (PRC), where Fe only scored >0.5 in the stream and river PRC (Chapter 4). However, on looking at the effect sizes, generally greater increases in Fe concentrations were found in surface- and pore-water, confirming that reduction of Fe$^{3+}$ in surface peats as WTD rose following restoration, was an important mechanism. Although there may also have been Fe in mineral inputs to streams relating to mechanical disturbance.

The same statistical testing procedures applied to Al, which was only tested with univariate statistics in streams and rivers for being a key stream water quality parameter. However, on analysing the stream Al data, we attributed increased Al to forestry/ access track disturbances, rather than restoration. Despite this, some increases following restoration (~2-fold) were found in pore and surface water plots following restoration, which may have been related to mineral soil disturbance.

The implications of water quality changes in streams are greater if this translates into rivers, which are nationally important spawning sites for Atlantic Salmon populations, subject to the EU WFD statutory water quality monitoring or occasionally used as a drinking water source. As we found no significant changes in WFD or drinking water standards, our results show that current levels of forest-to-bog restoration did not translate into significant impacts in river water quality. We can attribute this to a small proportion of the river catchment areas, which underwent restoration and dilution of impacted stream water in rivers (Rodgers et al., 2010). However, as forest-to-bog restoration continues to be carried out in the Rivers Dyke and Halladale catchments, there is the potential for existing and new restoration areas together to impact upon river water quality.
Figure 7.1: Conceptual diagram of main water quality and hydrological changes following drainage and afforestation and restoration of blanket bog
Figure 7.1 (continued): This figure is updated from chapter 1 (Figure 1.3) to include the changes in chemistry following restoration measured in this study, which were previously identified as gaps. The focus here is on surface- and pore-water chemistry, which was affected more by restoration than streams (Table 7.1).

Another effect which was observed at multiple scales (pore-, surface- and stream-water) was that of seasonality. All increases in water chemistry parameters following forest-to-bog restoration occurred from summer 2015, regardless of which restoration site they were measured on. For example, in DK2 restoration began in October 2014, while in DK6 the first felling was not until March 2015 but both sites showed similar temporal concentration changes. This has commonly been observed in other studies of felling on blanket peatlands (Cummins and Farrell, 2003a, 2003b; Ryder et al., 2014; Muller et al., 2015).

When looking specifically at the impact of increasing DOC concentrations in pore-, surface- and stream-water, the main implication was for aquatic carbon export. We observed a 31-39% increase in DOC concentrations, post-restoration compared to pre-restoration in impacted streams. This percentage increase was the similar from both Chapter 4 (n=4 streams, monthly sampling, +31%) and Chapter 5 (n=1 stream, intensive sampling, +39%) but in both cases was not significant relative to forest or open bog control catchments (which saw < 9% change between pre- and post-restoration periods). However, this did not result in significantly higher DOC export post-restoration in the restoration catchment compared to the controls; both the open bog and restoration catchments saw increased discharge (and carbon export) in the post-restoration year (2015), despite 28% less precipitation being recorded (Chapter 5).

We also confirmed the importance of storm events, which increase DOC export through both discharge and concentration increases. Other studies have shown the importance of storm events in nutrient export, as the period when the greatest losses from felled areas to downstream systems occur and that which is most difficult to mitigate against with the use of buffers (Rodgers et al., 2010; Asam et al., 2014b; O’Driscoll et al., 2014a, 2014b).

Thus, both precipitation patterns and the catchment response are important for solute export in general.

The catchment response to precipitation is strongly related to restoration of WTD following restoration (Wilson et al., 2010, 2011b). We observed a significant increase in
WTD, the first year post-restoration, after drain blocking and felling were carried out. However, felling trees alone can increase WTD and has been attributed to reduced transpiration from trees (Finnegan et al., 2014b). Given the limited amount of drain blocking at our sites, reduced evapotranspiration is likely be the main cause of WTD rise in our study. Re-wetting can also result in DOC, Fe and phosphate release from ombrotrophic peats (Fenner et al., 2001, 2011; Asam et al., 2012a), contributing to the concentration increases we observed in Chapter 3. In contrast, recovery of WTD over the longer term (0-17) was slower compared to the short term (0-1 years) and did not completely recover to open bog levels, 17 years post-restoration (Chapter 6). This has been found by others in the restored of drained afforested peatlands (Haapaléhto et al., 2011, 2014) and suggests further management interventions, or more time may be required, which we address in section 7.5.

Along with WTD, we measured the long-term recovery in water chemistry in formerly afforested blanket bogs having commenced forest-to-bog restoration. We found that some variables, showing concentration increases in the short term (phosphate and K) recovered by three years, while others (NH$_4^+$), which peaked later after restoration (three years) did not. This may present a barrier to recovery for bog plants specifically *Sphagnum* spp., which are less tolerant to excess nutrients (Bubier et al., 2007; Xing et al., 2011), along with a legacy of excess Ca in restoration sites up to 11 years post-restoration, which can also impair *Sphagnum* growth (Spatt and Miller, 1981).

We conclude this section by stating impacts of forest-to-bog restoration were mainly on DOC and plant nutrients (N, P, K), although some metals were also affected (Mn, Fe, Al, Ca). There was little evidence of effects on river water quality, although this may change with continued restoration within the catchment, depending how rapidly the impacts of earlier phases of restoration decline. This also applies to the export of aquatic carbon where there were strong hydrological effects of precipitation and discharge. The incomplete recovery of WTD and longevity of increased NH$_4^+$ in porewater may contribute to a slower recovery in bog vegetation in the longer term.
7.6 Recommendations for management

We tested the effects of restoration of formerly drained and afforested blanket bog by drain blocking, felling and harvesting on water quality. Thus, from our study we can make some management recommendations, widely applicable to the management/ restoration of afforested peatlands.

We attributed limited effects on streams and no significant effect on rivers to the catchment area felled (3-23% streams and <3% rivers), combined with the level of impacts following restoration. The catchment area felled has been found as a strong influence on stream chemistry in several other studies of felling on peatland (Nieminen, 2004; Rodgers et al., 2010; O’Driscoll et al., 2013), with one study (peat and mineral soils), recommending 30% as a threshold before significant effects on stream chemistry occur (Palviainen et al., 2014). Nevertheless, our study found a significant increase in phosphate and Fe in streams while felling between 3 and 23% of the catchment. Therefore, we do not provide a ‘no effect’ percentage threshold but advise that felling similar percentages of drained afforested peatland catchments can limit the impacts on stream water. Felling a larger percentage will likely have greater impact, thus a strategy might be to phase restoration over time to reduce impacts on water quality, bearing in mind that each restoration area may affect streams for 2-4 years (Cummins and Farrell, 2003a; Rodgers et al., 2010). However, we also acknowledge the importance of site specific factors – we observed increases in Al in streams (at afforested control and restoration sites) where there was shallower peat and a gravel/ sand road close-by. Although this was attributed to restoration, it is an example of where land management combined with site-specific factors can alter concentrations of key water chemistry varaibles.

The use of drain blocking, which in our study sites was limited to the downstream section of main collector drains, was effective in preventing significant increases in SPM and POC. However, in aiming to restore WTD more effectively in the longer term, blocking of the whole collector drain is recommended, and blocking of the plough furrows is a further enhancement, found to speed up recovery of WTD in other studies, in the first five years (Anderson, 2010). Although overall moisture conditions (indicated by plants) at the oldest restoration site may have recovered, further re-wetting may also help recovery of other restoration outcomes (Hancock et al., in prep.). Thus, we suggest plough furrow blocking as a measure to enhance restoration, especially on sloping sites >3% (Hancock
et al., 2014). In doing this, the impacts on water chemistry may be slightly altered, due to release from re-wetting (stimulated decomposition) of DOC and phosphate but there may be reduced export to streams as more water will be retained within the restoration site.

In Chapter 3, we studied both the so-called “standard fell” and “enhanced fell” methods of tree removal, where enhanced fell, resulted in harvesting of the main stems and brash (tree tops and branches) and standard fell, harvested only the stems, leaving brash arranged in “brash-mats” (for machinery to drive on) on-site.

Despite a larger initial impact on surface water, we suggest that signs of recovery in some pore- and surface-water chemistry variables (DOC, P, K) by the late autumn (December 2015) are a positive result for enhanced felling, while standard felling had less signs of this recovery. In order to determine the best method, it would be necessary to monitor the trajectories of both treatments in future years, which we discuss in section 7.6.

However, evidence from both our own studies (Chapter 3, Appendix 3.2) and the wider literature confirm that the decomposition of conifer brash and needles is a source of DOC, P, K, N (Hyvonen et al., 2000; Palviainen et al., 2004a, 2004b; Moore et al., 2011; Asam et al., 2014a, 2014b). Therefore, the removal of brash as carried out in ‘enhanced’ felling is likely to be the best method, by removing a major source of these nutrients, which were key to both short-term impacts on pore-, surface- and stream-water and to recovery-to-bog in the longer term. We conclude this section by recommending small fell areas, drain blocking, brash removal as practical and effective measures in the restoration of drained, afforested blanket bogs.
7.7 Future work and research highlights

7.7.1: Future work

We now propose future research, which can help build upon the findings of our study and further inform the future management of drained, afforested bogs.

7.7.1.1: Determining the best method of forest-to-bog restoration

The standard and enhanced fell treatments used in the Dyke Forest were designed to restore the bog, by removing large (>10 m) trees, making use of the timber, testing the effect of removing brash on recovery, and (as a later addition) the use of furrow blocking - applied in 2016. The results one-year post-restoration already show interesting patterns as sharp increases in surface water concentrations of DOC, nutrients and metals from enhanced felling and a slower release from standard fell plots. The most pressing research question is therefore: how does pore- and surface-water chemistry change in the longer-term as recovery to bog progresses in each of the restoration treatments? We recommend monitoring this annually up to five years post-restoration with then less frequent monitoring up to 20 years post-restoration. Another very useful and interesting question will be the effect of furrow blocking (applied 2016, to half of the restoration plots) and how it interacts with the standard and enhanced fell treatments.

7.7.1.2: Measuring restoration progress across a chronosequence of formerly afforested blanket bogs

In our study, we have used surface- and pore-water to assess the recovery in a chronosequence ranging from recent restoration sites (0-1 year post-restoration) to older restoration sites (17 years post-restoration). This study suggested some key changes in plant nutrients and metals over time, with implications for the recovery of bog vegetation. We now propose a wider study of the recovery process in restoration sites, integrating measurements of pore- and surface-water chemistry, water table, vegetation, mineralisation rates of nutrients and GHG measurements, adopting the techniques applied by our work and that of related studies (Chapter 6; Hancock et al., in prep.; Anderson, 2010; Andersen et al., 2013; Nwaishi et al., 2016). We propose this by space-for-time substitution on standard sites (e.g. fell to waste) and enhanced sites (harvesting stems plus brash, furrow blocking). This process will enable the identification of key thresholds in
time and processes, which will help speed up and improve recovery in formerly afforested blanket bogs.

7.7.1.3: Integration of the aquatic and gaseous effects of restoration on formerly afforested blanket bogs

We have measured the short term effects of forest-to-bog restoration on aquatic carbon export and showed that this was not significantly affected in the first year post-restoration. However, as the majority of the peatland carbon cycle comprises the gaseous exchange, the result of aquatic carbon should be combined with measurements of GHG emissions (Hermans et al., 2014), to give a complete carbon balance of recent restoration sites in comparison to afforested and open bog controls. This will help determine the impact of forest-to-bog restoration in the short term, where there is a disturbance to biogeochemical cycling. It is important to consider the short-term (disturbance related) losses before the system begins to recover towards that of an open bog. Ultimately, the integration of aquatic and gaseous carbon measures on older restored sites will be important to consider along with measures on afforested and open bog sites to determine which state (forest or bog) is best for climate cooling, and how restoration sites compare with them (Hambley, 2016).

7.7.1.4: Effective buffer strips for mitigation of phosphate and Al leaching to streams in formerly afforested blanket bogs

Our results showed significant increases in phosphate in streams, which at the current scale of restoration did not significantly impact on rivers. Associated physical disturbances may also have increased Al concentrations at some stream sites. In catchments where larger peatland areas are felled/undergo restoration, there may be impacts upon river systems which could change the status of mandatory water quality standards or impact upon biodiversity, such as Atlantic salmon. Several studies have seeded the grasses Holcus lanatus and Agrostis capillaris in buffer zones, which have been used effectively (in various designs) to remove phosphate from runoff (Asam et al., 2012b; O’Driscoll et al., 2014a, 2014b). However, these grasses are not suitable vegetation in designated SAC blanket bogs, which are around our study sites and are therefore not suitable for introduction here. Given that there has also been some potential in plants to remove Al from water (Bakar et al., 2013), we propose future research to
determine if species occurring naturally can be used to partly mitigate against leaching of phosphate and Al to streams, in forest-to-bog restoration sites.

7.7.2: Research highlights

In this study we have:

1. Provided the first comprehensive study of the short term impacts of restoration by felling and drain-blocking, on formerly drained blanket bogs, afforested with non-native conifers, by:
   - Conducting a large scale, replicated study of pore- and surface-water at multiple restoration sites and controls
   - Monitoring the effects on stream and river water quality at a monthly timescale pre- (15 months) and post-restoration (15 months), in comparison to control sites and catchments
   - Estimating the effects of restoration on aquatic carbon export in a catchment undergoing restoration, compared to afforested and open bog controls
   - Assessing the effects of forest-to-bog restoration at multiple scales

2. Studied for the first time the long-term effects of the restoration process through space-for-time substitution (0-17 years post-restoration) using pore- and surface-water to assess recovery in formerly drained and afforested blanket bog restoration sites

3. Concluded with recommendations for the restoration of drained blanket bogs afforested with non-native conifers for:
   - Minimising the impacts on water quality
   - Improving recovery to bog function
Appendices

Appendix 3.1 – Leaching of DOC from Apollo frost fleece®

Rationale:
Piezometers were used for sampling pore water. These were lengths of 32 mm (internal diameter) polypropylene piping cut to length for either shallow pore water sampling (40-60cm) or deep pore water sampling (90cm). To allow collection of the pore water, a 10 cm screen of holes was drilled in each piezometer consisting of lines of 3 mm holes spaced 1 cm apart in alternately matched lines. Commonly in peat pore water sampling – the screen is covered with a fabric or plastic gauze to prevent peat clogging the holes e.g. (Haapalehto et al. 2014). As plastic gauze is expensive, a cheaper but suitable alternative was proposed. Apollo frost fleece® (AFF) is designed for gardening to provide heat insulation to growing plants, but allow precipitation to pass through. As AFF was also strong and cheap it may be a suitable alternative. However, there were no previous reports of its use in water sampling; therefore, it was useful to determine its potential for leaching chemical parameters which were being measured in the study of pore water chemistry (Chapter 3). As AFF was made from plastic fibres (carbon), this leaves potential for leaching mainly of dissolved organic carbon (DOC).

Aim:
To test the ability of Apollo frost fleece® (AFF) to leach DOC and other chemical parameters

Methods:
To determine the potential for AFF to leach chemicals to water two experiments were conducted. Experiment A looked simply at the change in water chemistry after passing through the fleece to replicate field conditions (as pore water passes through the fleece into the piezometer. Experiment B was a more prolonged exposure (24 hours) on a laboratory shaker to give a longer more rigorous contact between the fleece and water. Although this would not happen in the field it allowed consideration of what could additionally be leached from the fleece. Both experiments were carried out with Milli-Q water (18.2 MΩ resistivity), which has almost all DOC removed and River Dyke water
(as a similar composition to field conditions). In both experiments, samples were measured for DOC concentrations (University of Aberdeen) and conductivity as described in Chapter 2.4. Conductivity as a summative measure of dissolved ions (Vogt et al., 2010), was used a tracer to determine total quantities of any other chemical parameters which had been leached from the fleece.

**Experiment A:**

A rectangle of AFF (13x15cm; used for piezometer screen covers) was placed in a plastic filter funnel. 200mL of water was passed through the funnel and collected in a clean plastic bottle. A further 500 mL was passed through the filter and discarded to represent re-wetting in between sampling. A final 200 mL sample was then passed through and collected. These experiments were run in triplicate for both Milli-Q and river water. Control experiments were carried out, without AFF placed in the funnel.

**Experiment B:**

One AFF rectangle (13x15cm) was placed in 150 mL of water and left on an orbital shaker for 24 hours. These experiments were carried out in triplicate for both Milli-Q and river water. Control experiments were carried out without AFF. This was then repeated with the same fleece and fresh water for a further 24 hours.

For both experiments all samples were measured for conductivity. For DOC measures, samples were filtered under vacuum through 0.7 µm GFF filters (Chapter 2.5.1) and refrigerated at 4°C, before posting (in ice box) to University of Aberdeen for analysis. Results of both DOC and conductivity were compared between control and treatment for each experiment, using the Mann Whitney test function `wilcox.test`, (package `stats`, R Core Team, 2016). Results for both repeats from each experiment were combined for statistical analysis.

**Results:**

There were no significant differences in conductivity or DOC from experiment A. In experiment B (shaking), there were significant differences in both conductivity and DOC from using the Milli-Q water, thus the fleece caused a slight increase in both DOC and conductivity. In the experiment B (shaking), using river water concentrations of DOC, were not significantly different between control and treatment. However, there was a
slight increase in conductivity, with the treatment mean 11 µS cm\(^{-1}\) higher than the control.

**Table A3.1.1: Mean ± SE conductivity and DOC concentrations of Apollo frost fleece® (AFF) leaching experiments for controls and treatments.** Results shaded grey were significantly different between control and treatment

**Conclusion:**
These experiments confirmed that passing water through frost fleece (replicating field conditions) did not significantly increase concentrations of DOC or conductivity, when using Milli-Q or river water. Despite some significant differences in the shaking experiment with Milli-Q water, the change in DOC concentrations was small compared to concentrations in river water (and pore water). For the shaking experiment with river water, the increase in conductivity was significant. However, this experiment did not represent field conditions, only the potential for leaching from frost fleece. The increase was also a smaller percentage of pore water conductivity (≤10 %; Table 3.2). As the AFF was applied to all piezometers, any leaching from AFF into pore water samples was assumed to be consistent across all plot classes; therefore, no correction was required to field data.
Appendix 3.2 – Experiments of DOC, nutrient and metal leaching from peat, needles and brash

Rationale:
It was hypothesised that following forest-to-bog restoration, there would be significant increases of DOC, nutrients and metals in surface and pore water. Decomposition from brash and needles left on site was one of the primary reasons for this, as it is well known from the literature that brash and needles release can DOC, nutrients and metals (Palviainen et al., 2004a, 2004b; Moore et al., 2011; Asam et al., 2014a, 2014b). Therefore, to supplement measures in the field and determine, what is leached from brash and needles from our study sites, laboratory leaching experiments were carried out.

Aim:
To test the potential for peat, needles and brash to leach DOC, nutrients and metals into surface and pore water under laboratory conditions.

Methods:
Surface peat cores were collected from afforested sites (using 400g size aluminium soup cans, rinsed thoroughly and soaked overnight in 2% Decon90®, along with fresh branches taken from Sitka spruce and Lodgepole Pine trees. These were placed into plastic columns (n=5) either as peat only (P), peat + needles (P+N), peat + needles + brash (P+N+B). Plastic columns were constructed from PVC tubing (internal diameter 7.0 cm) cut to length and drilled to allow sampling from the peat layer (2cm and 7cm from base), the needle layer (11cm from base) and brash layer (14cm from base). Flexible PVC tubing was attached to each hole for sampling with a syringe. Columns were sealed at the bottom by using glass petri dishes inserted into the bottom of the column and sealed with layers of Gaffatape®. As some seals were not completely water tight, columns for the P and P+N treatment were remade from PVC sample bottles, where the tops were removed to resemble columns.

In each column a peat core was added (8 cm height). As the P treatment had no needles or brash, this was essentially a control treatment for the brash and needles but also allowed
determination of what was leached from surface peat. The P+N treatment had a 4 cm covering of needles picked from branches. While the P+N+B treatment had a 4 cm needle layer and a 15 cm brash layer (branches with needles cut into ~5 cm lengths to fit inside columns). The mass of each layer was weighed.

Precipitation collected in July and August 2015, from Dyke Forest locations (Figure 3.1) and the Environmental Research Institute (Thurso), was used in each experiment. Precipitation was filtered through 0.7 µm GFF filters to remove debris and combined for use in column experiments, as a limited volume was available during these months.

400 mL of precipitation was added to each P+N+B treatment column and 200 mL was added to the P and P+N treatment columns. This was due to the limited volume of precipitation collected. Precipitation was left in the column firstly for a 24-hour incubation. Water samples were collected from the peat, needle and brash layers respectively and pH and conductivity was measured from a subsample. The remainder of the sample was filtered for measurement of DOC, nutrients and metals as described in Chapter 2.5.1. Columns were sampled top down, so that the precipitation remaining in each layer was sampled from that layer. The experiment was then repeated for a nine-day incubation.

Separate experiments were conducted for each tree species (Sitka spruce and Lodgepole Pine), each time collecting fresh branches and peat cores. However due to a limited number of samples being collected from each column (with sufficient volume to measure all variables), results from both species were combined. The column experiment was set up to represent field conditions following forest-to-bog restoration after precipitation. 15 cm of brash was chosen as a typical brash depth measured in forest-to-bog restoration plots adjacent to where cores were collected. Samples from the peat layer represented shallow pore water, which was collected from a layer of peat with needles and brash on the surface (P+N+B treatment). While in the P+N treatment this was shallow pore water from peat covered in needles and the P treatment was peat from an afforested site with no additional surface cover. Samples collected from the needle and brash layers in the column, were representative of surface water (drainage ditches), which had been filled with brash and needles, following restoration. In field conditions, brash did end up in ditches after restoration but not as densely as in columns. However, this experiment was designed primarily to test whether each of the materials (peat, needles and brash) could
potentially leach DOC, nutrients and metals with the aim to aid interpretation of the real field measurements, made across a range of forest-to-bog restoration sites.

Figure A3.2.1: Peat, needle and brash experiment columns showing (a) peat + needle + brash treatment (P+N+B) and (b) peat + needle (P+N) treatments. (b) is the earlier design where columns initially leaked into petri dishes and were replaced by bottles.

Statistical analysis was carried out using generalised linear models (GLMs; function glm, package stats, (R Core Team, 2016), to test for differences in concentrations of DOC, nutrients and metals, between precipitation, the peat layer in each of the treatments (P, P+N, P+N+B) and the needle and brash layers (P+N+B treatment). This was carried out following the protocol in Chapter 3.2.6 also used for field data. Statistical analysis for the peat, needles and brash experiment data were performed on the most important water
chemistry variables found to increase in the field post-restoration: DOC, K, phosphate, NH$_4^+$, Mn and Al. These were also generally the most affected water chemistry variables across the forest felling literature.

**Appendix 3.3 – Precipitation chemistry.** Boxplots of range in concentrations and mean (●) for each water chemistry variable measured in this study for precipitation collected in two open bog locations at the north and south sides of the study site (Figure 5.2). Samples collected from Feb 2015 to Jun 2015 and in Dec 15 (data from Jul to Nov 15 omitted due to contamination of precipitation samplers).
Appendix 4.1: Summary of models testing for significant changes in pass rates of water quality standards (WFD and drinking water) following forest-to-bog restoration, using mixed models. Wald chi-square tests of the model fixed effects were carried out to determine if the interaction term was significant. Thus we used primarily the treatment*period interaction to test for an effect of restoration (p<0.05), for which we found no parameters significantly affected. (*) in the table indicates parameters, for which mixed models could not converge and instead ordinary generalised linear models were used instead.

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</tr>
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<tbody>
<tr>
<td>Al</td>
<td>binomial</td>
<td>logit</td>
<td>4.21</td>
</tr>
<tr>
<td>Fe</td>
<td>binomial</td>
<td>logit</td>
<td>1.76</td>
</tr>
<tr>
<td>Cu</td>
<td>binomial</td>
<td>cloglog</td>
<td>1.62</td>
</tr>
<tr>
<td>Mn</td>
<td>binomial</td>
<td>logit</td>
<td>2.35</td>
</tr>
<tr>
<td>Ni</td>
<td>binomial</td>
<td>logit</td>
<td>0.00</td>
</tr>
<tr>
<td>Turbidity</td>
<td>binomial</td>
<td>logit</td>
<td>2.21</td>
</tr>
</tbody>
</table>

significant interaction (p<0.05) = effect of restoration
## Appendix 5.1: Stream depth logging instrumentation and discharge measures

<table>
<thead>
<tr>
<th>Catchment</th>
<th>Restoration</th>
<th>Afforested</th>
<th>Open bog</th>
</tr>
</thead>
<tbody>
<tr>
<td>Logger model</td>
<td>Isodaq 2e data logger - Nov 2013 – Mar 2015</td>
<td>Druck 1830 pressure transducer and thermocouple connected to Campbell 21X logger - Oct 2013 - Dec 2015</td>
<td>Level TROLL 400 (In Situ Inc.)</td>
</tr>
<tr>
<td></td>
<td>Rugged TROLL 100 data logger (In Situ Inc.) - Apr – Dec 2015</td>
<td></td>
<td>Level Baro TROLL*</td>
</tr>
<tr>
<td>Temperature</td>
<td>Intermittent record</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Discharge measures by flow meter</td>
<td>( n \approx 13 )</td>
<td>( n \approx 13 )</td>
<td>( n \approx 2 )</td>
</tr>
<tr>
<td>Discharge measures by salt dilution</td>
<td>( n=14 )</td>
<td>( n=9 )</td>
<td>( n=13 )</td>
</tr>
<tr>
<td>Stilling well</td>
<td>PVC tube of 5cm diameter with 0.5cm holes drilled every 10cm of length</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*1 Baro TROLL measures atmospheric pressure used to correct absolute pressure measured at afforested and restored catchments

*2 Late choice of bog control catchment

Originally a larger bog control catchment was selected (812 ha), although no storm sampling was carried out in this period (Oct 2013 – Apr 2014) due to both depth logger and autosampler malfunction. Access to this catchment was also unsuitable for frequent short notice storm event work. Considering these issues (along with the catchment being too large for comparison with restoration and afforested catchments -chapter 5.4.5), a more suitable bog control was chosen in April 2014, with access to a working depth and temperature logger. Hence water sampling commenced from bog catchment from April 2014.
Appendix 5.2: Summary of all storm events sampled. Stage, discharge, precipitation, lag time and samples collected. Grey shading is period of forest-to-bog restoration management. Red shading is sampling events which were not classified as storms – stage rise < 10cm in restoration catchment.
Appendix 5.3: Monthly precipitation and discharge 2014-2015: monthly precipitation (a), number of rain days (>0.1 mm) (b), and mean discharge (c) during 2014 and 2015 in the open bog catchment. Precipitation data from Ed Turner (NERC Pools project).
Appendix 5.4: Monthly precipitation (a), number of rain days (>0.1 mm) (b), from 2012 to 2015 in the open bog catchment. Data from Ed Turner (NERC Pools project), Pete Levy (CEH).
9. References


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