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The effect of peatland rewetting on gaseous and fluvial carbon losses from a Welsh blanket bog

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The Effect of Peatland Rewetting on Gaseous and Fluvial Carbon Losses from a Welsh Blanket Bog

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PhD Thesis

School of Biological Sciences

Bangor University

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Finally, I dedicate this thesis to three people: firstly to my parents for their encouragement and support throughout my education, as well as grounding in me a love for the outdoors which seems a pre-requisite for enjoying rainy fieldwork days on the Migneint. Secondly, I dedicate it to my wife Susan for her love and support.

Summary

Throughout the last two centuries large areas of northern (i.e. not tropical) peatlands have been subject to extensive drainage, typically carried out through the digging of ditches. Ecosystem restoration now focuses on blocking these ditches, with various aims such as increasing biodiversity or sequestering carbon. Despite the increasing number of restoration projects taking place, there are still large knowledge gaps concerning the effects of ditch blocking on biogeochemistry. This thesis presents the results from a ditch blocking experiment on a Welsh blanket bog, and compares two methods of ditch blocking: damming using peat dams, and a reprofiling method that uses peat dams as well as infilling the ditch.

Following ditch blocking, results suggested that water tables had risen by approximately 2 cm. Post-rewetting CH_4 fluxes increased substantially, with blocked ditches (and pools within blocked ditches) releasing large amounts of CH_4. This increase was most notable for reprofiled ditches, although fluxes from dammed ditches were also larger than those from unblocked control ditches. Upscaling CH_4 fluxes to the catchment area suggested that before rewetting the catchment-scale flux was 2.89 g CH_4 m^{-2} yr^{-1}. Post- rewetting fluxes were calculated as 3.55 g CH_4 m^{-2} yr^{-1} if all ditches were blocked using a damming method, and 4.21 g CH_4 m^{-2} yr^{-1} if all ditches were blocked using a reprofiling method. A detailed survey of bog pools that formed behind ditch dams showed that *Eriophorum* species colonised shallower pools (< 50 cm depth) whilst *Sphagnum* species dominated in deeper pools. Considering that *Eriophorum* is well-documented as a species associated with high CH_4 fluxes, and that certain *Sphagnum* species have been observed to consume CH_4, we argue that deeper pools are desirable to facilitate the colonisation of preferential plant species that might have the capacity to mediate large post-blocking CH_4 fluxes.

In addition to CH_4 fluxes, we also present a limited amount of carbon dioxide (CO_2) flux data, obtained using static chambers in conjunction with an infra-red gas analyser. Results were very variable but CO_2 uptake from *Sphagnum* within unblocked ditches was extremely high, and this therefore suggests that *Sphagnum* colonisation is a favourable outcome for both a CH_4 and CO_2 perspective.

A certain degree of the low soil decomposition rates that are found in northern peatlands has been attributed to constraints on the activity of the extracellular enzyme phenol oxidase, and the associated 'enzymic latch' mechanism. To test how extracellular enzymes respond to drainage and ditch blocking, soil samples were analysed from three different sites

on the Migneint. The results from one site suggested that historical peatland drainage had stimulated phenol oxidase activity and enhanced hydrolase activities in comparison to enzyme activities at an undrained site. Results from a second drained site showed no change in phenol oxidase activity, but a decrease in hydrolase activity compared to the undrained site. We hypothesised that this was due to vegetation differences at the second site; that large areas of *Juncus* and *Eriophorum* were supplying low-molecular weight root exudates to the soil, thus negating the demand for hydrolase enzymes that are responsible for the production of low molecular weight compounds. Following ditch blocking there was no evidence of changes to enzyme activities, implying that activities remain enhanced as a legacy of previous, drained conditions.

The effect of ditch blocking on water chemistry was examined through regular sampling of ditch water, pore water, and overland flow (OLF) water. For ditch water there was no difference between treatments in the concentration or composition of dissolved organic carbon (DOC), particulate organic carbon (POC) concentration, pH, electrical conductivity (EC), or sulphate concentration. For pore water there was some evidence for higher DOC concentrations associated with blocked ditches occurring in summer 2011. This enhancement occurred one month before an increase in DOC concentration in the stream draining the blocked catchment (relative to an unblocked control catchment). These results suggest that ditch blocking stimulates a brief flush of DOC from a catchment, possibly due to ecosystem disturbance during the physical act of rewetting. Although there was no effect of rewetting on OLF water chemistry, we noted that the concentrations of DOC in OLF were very similar to ditch water DOC concentrations. As such, we hypothesise that ditch blocking diverts water out of ditches, resulting in increased OLF. We therefore suggest that ditch blocking studies must measure this pathway, as previous work has largely ignored it.

In addition to elucidating the effects of ditch blocking, investigations into the use of spectrophotometric proxies for DOC were undertaken. These investigations consistently showed that light absorbance at 254 nm is a more accurate and reliable proxy than 400 nm. We also propose a new DOC proxy, the concentration of phenolic compounds in a water sample, and show how this compares to traditional light absorbance proxies.

Contents

Introduction

1.1. Overview

Northern peatlands are vitally important ecosystems that fulfil many key functions, the most important of which is carbon storage. Gorham's (1991) oft-cited figure is that this store amounts to 455 Pg of carbon, but recent (and conservative) calculations have suggested 547 Pg (Yu *et al.*, 2010). Considering that peatlands occupy less than 3% of the total land surface of the Earth (Charman, 2002) this is a sizeable amount, contributing to approximately 15-33% of the global carbon store (Gorham, 1991, Botch *et al.*, 1995, Turunen *et al.*, 2002, Joosten & Clarke, 2002). Additionally, peatlands store 10% of global freshwater (Joosten & Clarke, 2002). Furthermore, the biodiversity of such habitats is very high, and numerous species of plants and animals are restricted to them (Warner & Asada, 2006, Renou-Wilson *et al.*, 2011) and therefore they have considerable conservation importance.

Smith *et al.* (2004) suggest that northern peatlands have been long-term net sinks of carbon dioxide (CO_2) and net sources of methane (CH_4) for around 10,000 years. Pristine peatlands are generally net sinks of carbon (Limpens *et al.*, 2008, Bridgham *et al.*, 2006, Worrall *et al.*, 2003, Rivers *et al.*, 1998) but can be net sources during some years (Waddington & Roulet, 2008, Roulet *et al.*, 2007). The other main loss of carbon from peatlands is in the form of dissolved organic carbon (DOC), which is exported in drainage waters.

Restoration ecology, as a discipline, was outlined by Aber & Jordan (1985) as a tool that could "provide a framework for this systematic study and reconstruction of communities and ecosystems", "broaden the scope of ecology", and pave the way for the "generalization and simplification of ecological theory". Due to the degradation they suffered many peatlands are prime candidates for restoration. In the UK this degradation took the form of drainage ditches (also called 'grips' or 'drains') which were dug during the 19th and 20th centuries, when such areas were viewed as useless wastelands (Johnston & Soulsby, 2000), and largely stopped in the mid-1980s when subsidies ended (Ramchunder *et al.*, 2009). The aim of digging ditches is to lower the water table (Hillman, 1991, Rothwell *et al.*, 1996, Price, 1997), although Rothwell *et al.* (1996) noted that ditch spacing does not control soil water content, and Stewart & Lance (1991) argued that drainage in the UK did not actually improve the land in the intended way for either agricultural grazing or for the management of game birds for hunting.

Drainage leads to a sustained net source of CO_2 (Rowson *et al.*, 2010, Salm *et al.*, 2009). Generally, drainage and drought decrease CH_4 emissions and increase CO_2 and N_2O emissions (Alm *et al*., 1999, Martikainen *et al.*, 1995, Glenn *et al.*, 1993, Freeman *et al.*, 1993). CO_2 fluxes increase as conditions become more favourable for aerobic metabolism (Freeman *et al.*, 1993) whilst CH_4 fluxes decrease because the increased aerobic zone is less suitable for methanogenic archaea and, to a lesser extent, more suitable for methanotrophic bacteria (Freeman *et al.*, 2002). With regards to changes in DOC dynamics, increasing the extent of the aerobic zone causes a large store of microbially-generated DOC to be produced that is then flushed out after precipitation events (Mitchell, 1991, Waddington *et al.*, 2008). There is also some debate about whether drainage can cause increased flood peaks downstream, and this probably depends on the characteristics of both the ditching and the peatland (Holden *et al.*, 2004).

Much of the peatland drainage in the UK occurred on blanket bogs, which are fundamentally different to other peatlands. Blanket bogs exhibit complex topography, and on a landscape scale can extend across a range of altitudes and slope gradients (Graniero & Price, 1999). Vegetation typically includes species such as *Calluna vulgaris*, *Eriophorum vaginatum*, *Empetrum nigrum*, *Erica tetralix*, *Juncus squarrosus*, *Vaccinium myrtillus* and *Sphagnum* species (Tallis, 1969). Blanket bogs are largely ombrotrophic, and often found at the headwaters of river catchments, making them important sources of potable water. The quality of water draining these systems thus has relevance for aquatic ecosystem functioning (Karlsson *et al.*, 2009), water treatment costs (McDonald *et al.*, 2001), and human health issues as DOC can form carcinogenic byproducts (trihalomethanes) during water treatment (Chow *et al.*, 2003).

The low hydraulic conductivity of blanket bogs makes them more resistant to drainage compared to other peatlands (Boelter, 1972, Galvin, 1976, McDonald *et al.*, 1991). This can be observed easily: even when intensively ditched a blanket bog is wet underfoot, and modelling has suggested that water tables in blanket bogs are only significantly altered adjacent to the ditch, due to their low lateral hydraulic conductivity, and that beyond ten metres the drawdown is negligible (Price *et al.*, 2003).

The changes associated with drainage are completely different to those caused by the large-scale removal of vegetation associated with peat harvesting on an industrial scale, and from the full-scale land-use changes to intensive grassland and cropland associated with the drainage of many lowland peat areas. As such, the restoration (i.e. rewetting) of blanket bogs typically involves only the blocking or reprofiling of ditches, without the need for active

intervention to re-establish or to completely change the vegetation. Approximately nine percent of deep peats in Britain have been afforested with conifers (Cannell *et al.*, 1993), and for restoration to be successful these must be felled; ditch blocking alone is not sufficient (Anderson, 2010).

The main aim of ditch blocking is to return the water table to pre-drainage levels to encourage peat-forming species to flourish, although it can take many years for the hydrological regime to fully stabilise (Price *et al.*, 2003). Further aims are reduced DOC flux, reduced sediment transfer, and reduced erosion (Armstrong *et al.*, 2009). As of 2008 most UK restoration projects were focused on hydrology or ecology, with biodiversity consistently being used as a justification. Out of fifty four peatland restoration projects, carbon was cited as being "extremely important" in just three incidences (Holden *et al.*, 2008). Nevertheless, increasing the water table may lead to decreased total respiration (Urbanovä *et al.*, 2011, Tuittila *et al.*, 1999) thereby creating a new CO_2 sink (Waddington *et al.*, 2010, Komulainen *et al.*, 1999, Tuittila *et al.*, 1999), or a reduced source (i.e. avoided loss) (Waddington & Price, 2000). A negative side effect is that CH_4 fluxes rapidly increase, but may remain lower than those from pristine sites (Komulainen *et al.*, 1998). However, there is still considerable uncertainty concerning the magnitude of changes in gaseous carbon fluxes following rewetting, and more data is needed on the subject.

Numerous materials have been used to block ditches including heather bales, peat turves (the most widely used in the UK), plastic piling, Perspex, plywood, wooden planks and stones. Some aim to form a completely watertight dam, whilst others are designed to reduce water flow and stimulate the infilling of the drain (Armstrong *et al.*, 2009). Worrall *et al.* (2007) concluded that the method of drain blocking had no effect on water colour after experimenting with heather bales, piling, and turves. They therefore advocated the use of peat turves as the most economical. Armstrong *et al.* (2009), however, found that peat turves were only intermediate in terms of success, with over 5% of dams failing, and just under 60% being well blocked. A more advanced option is reprofiling, where peat (or another available material) is used to completely fill the old ditch line.

Despite the large body of research concerning drainage and restoration of peatlands there are still issues to be resolved. Bussell *et al.* (2010) show that few projects monitor pre-restoration baseline data. This is understandable to some degree; many ditch blocking projects will be undertaken by stakeholders such as water companies who may only have limited interest in monitoring (as well as a lack of funds), and a research programme by an academic institution may only be added at a later date. Alternatively, ditch blocking may

take place without any rigorous scientific justification, but simply because it is in vogue and a potential funding source is found to 'improve' the ecosystem. The data from such projects may be extremely limited, or nonexistent.

Another shared trait of many restoration projects is the use of a control site and a treatment site that may be quite geographically separated (Bussell *et al.*, 2010). Once again, this is understandable as many stakeholders will view the robustness of any scientific research as a secondary concern, and apply a blanket treatment (i.e. ditch blocking) across a whole site. Nevertheless, the use of two distinct sites produces additional confounding variables that may obscure treatment effects, due to possible differences in geology, vegetation, aspect, gradient, and historical management. Holden *et al.* (2004) point out that a combination of instrumentation and process-based monitoring of multiple ditch-blocking projects is needed to fully elucidate how future restoration should develop to be successful in a cost-effective manner.

This thesis aims to go some way to addressing some of these issues by using two years of field measurements at one primary experimental site, where both blocked (treatment) and unblocked (control) ditches are present in a randomised and replicated design. By only using one site, the aforementioned differences in having geographically distinct treatment and control sites is removed. A second aim of this thesis is to examine the way in which DOC is measured and modelled. As stated above, many projects will be constrained by monetary and practical limitations and, as such, various proxies are often used rather than directly measuring DOC concentrations. These are evaluated so as to provide useful analytical information for projects where limitations impose upon monitoring. The explicit aims of each experimental chapter are:

1) To determine if an empirical relationship exists between DOC and phenolic concentrations, and whether such a relationship can allow DOC concentrations to be calculated using phenolic concentrations as a proxy.
2) To fully investigate the use of UV-visible absorbance measurments as proxies for DOC concentration and DOC quality, and to assess how absorbance changes in samples under storage for three months.
3) To compare the activity of soil extracellular enzymes in pristine, ditched, and ditch-blocked peatlands.

4) To examine the effects of ditch blocking on water chemistry (DOC, particulate organic carbon, pH, electrical conductivity, sulphate) at both a ditch scale and a catchment scale.
5) To quantify the extent of vegetation colonisation in bog pools formed during ditch-blocking, and to determine if the vegetation composition of pools controls DOC concentrations.
6) To compare CH_4 fluxes from ditched and ditch-blocked blanket bog.

1.2. The field site

The primary field site is at the head of Afon Ddu catchment (latitude 52.97°N, longitude 3.84°W) above Ffynnon Eidda, on the Migneint blanket bog, in Snowdonia National Park, north Wales (UK). Several secondary field sites were used in addition to this (figs. 1 and 2). Blanket bogs form in areas that feature high rainfall and relatively low temperatures, and are typically found in northern locations such as the UK, Russia, and Canada. In Wales, their formation has been partially attributed to anthropogenic disturbance during Neolithic times (Moore, 1973). Blanket bogs are extremely common in UK uplands, and store large amounts of carbon (Holden, 2005). The altitude of the Afon Ddu fieldsite is 490 m above sea level and the aspect is north-northwest. According to the Soil Survey of England and Wales the soil is raw oligo amorphous peat. The geology consists of mudstone and siltstone (Lynas, 1973). Mean peat depth at the site is 1.32 m (n = 101, SE = 0.06, minimum depth = 0.31 m, maximum depth = 3.14 m). Mean annual air temperature is 8.6^{o}C and mean annual precipitation is 2200 mm (Cooper, 2013). Prevailing winds are from the west.

The Migneint is a Site of Special Scientific Interest (SSSI) and part of the larger Migneint-Arenig-Ddualt Special Area of Conservation (SAC). It is designated by the Joint Nature Conservation Committee as the second largest area of blanket bog in Wales after the Berwyns (JNCC, no date). The conservation importance of blanket bog is recognised by its inclusion in the European Habitats Directive. The vegetation of the Migneint includes areas of M18 (*Erica tetralix-Sphagnum papillosum*), M19 (*Calluna vulgaris-Eriophorum vaginatum*), and M20 (*Eriophorum vaginatum*) according to the JNCC National Vegetation Classification (NVC) (Elkington *et al*, 2002). The Mignient is a Special Protection Area (SPA) due to the presence of *Circus cyaneus* (hen harrier), *Falco peregrinus* (peregrine falcon) and *Falco columbarius* (merlin). The land is lightly grazed by Welsh mountain

sheep, generally at a rate of 0.05 LSU/ha/yr, and there is some history of burning for heather management (Evans *et al.*, 2008). There is limited evidence of peat cutting on a local scale.

Figure 1. Location of the field sites used in this PhD. 1) The Migneint, which includes Afon Ddu, Llyn Serw, Nant y Brwyn, Bryn Du, and Llyn Conwy, 2) Peaknaze, 3) Plynlimon, 4) Llyn Teyrn, 5) Llyn Cwellyn, 6) Bangor (site of fen mesocosms), 7) Alwen Reservoir. North is directly up. © Crown Copyright/database right 2012. An Ordnance Survey/EDINA supplied service

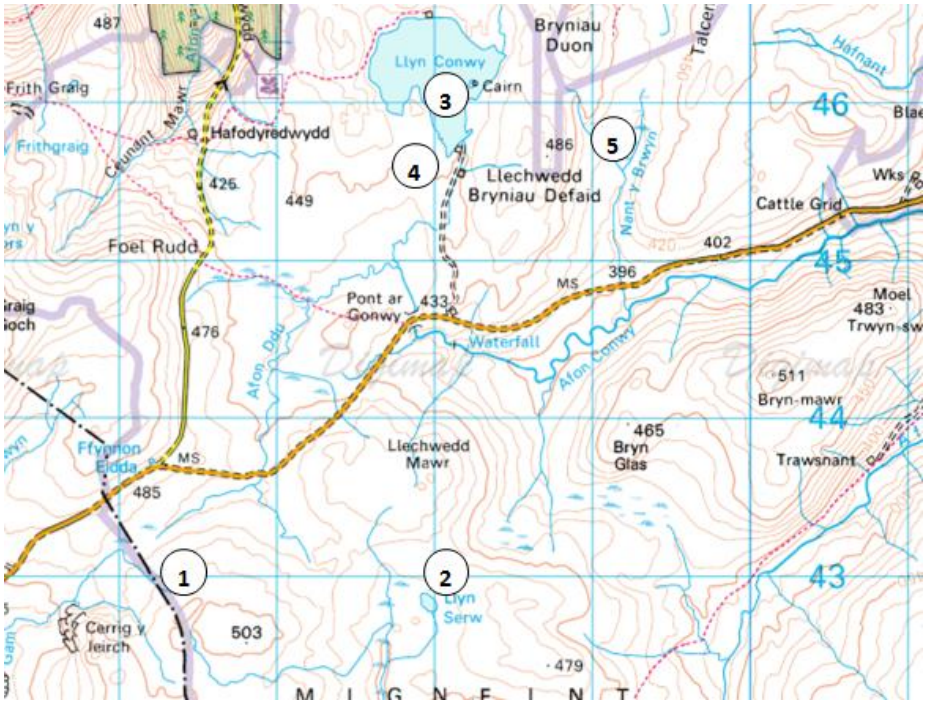

Figure 2. Location of the various Migneint field sites. 1) Afon Ddu (the primary field site), 2) Llyn Serw, 3) Llyn Conwy, 4) Bryn Du, 5) Nant y Brwyn. North is directly up. Each grid square is 1 km.. © Crown Copyright/database right 2012. An Ordnance Survey/EDINA supplied service

Numerous scientific work has taken places on the Migneint: it is one of the Centre for Ecology and Hydrology's (CEH) carbon catchments that attempt to quantify the full peatland carbon balance (Billett *et al.*, 2010). It has also been used extensively for both field-based experiments (e.g. Austnes *et al.*, 2010, Evans *et al.*, 2012) and laboratory-based core experiments (e.g. Kim *et al.*, 2008, Boardman *et al.*, 2011).

Approximately 26% of the Migneint (including the field site) is owned by the National Trust, as part of the Ysbyty Ifan estate, who lease the land out for grazing to tenant farmers. The other major stakeholder is Dŵr Cymru Welsh Water who manage Llyn Conwy, a Migneint lake, as a potable water supply. The River Dee also originates on the Migneint and is used as a potable water supply. As such, any management strategies that reduce DOC concentrations are of interest as a potential cost-saving measure in water treatment.

The Migneint has been subjected to intense drainage throughout the 19th and 20th centuries, with the most recent activity ending during the 1980s. This has been carried out through the digging of ditches, first using human labour and, later, using machinery. As such, observational surveys by the National Trust suggest that localised drying out around ditches is causing mire communities to transition to the dry heath community H12 (*Calluna vulgaris-Vaccinium myrtillus*). The same surveys show that some ditches have naturally been recolonised by moss species such as *Sphagnum fallax*. Ditch blocking on the Migneint was first undertaken by Dinsdale Moorland Services at the southern end of the SAC on Forestry Commission land as part of the RSPB Life Project. This was followed by ditch blocking on National Trust land at the Afon Ddu field site. This was again carried out by Dinsdale Moorland Services with additional support from local farmers, and as of June 2012 approximately 350 km of ditches have been blocked. The National Trust plan to continue restoration work until all ditches on their land have been blocked. This PhD follows on from an earlier research project that examined the effects of ditch blocking on carbon cycling on the Migneint (Cooper, 2013).

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Quantifying dissolved organic carbon concentrations in upland catchments using phenolic proxy measurements

2.1. Introduction

Dissolved organic carbon (DOC) is a fluvial export from organic rich soils. Its concentration is affected by various factors, such as soil carbon pool, peat cover (Aitkenhead *et al.*, 1999), hydrology (Dawson *et al.*, 2004), and vegetation (Palmer *et al.*, 2001), as well as autochthonous production (Hope *et al.*, 1994). DOC concentrations have been increasing in waters draining upland catchments in the UK (Freeman *et al.*, 2001a), with similar trends being observed in waters in North America (Stoddard *et al.*, 2003) and Scandinavia (Skjelkvåle *et al.*, 2005). One hypothesis is that these increases are driven by a recovery from atmospheric deposition (Monteith *et al.*, 2007, Ekström *et al.*, 2011, Evans *et al.*, 2012) although experimental studies also demonstrate that DOC loss can be strongly affected by climate (e.g. Fenner & Freeman, 2011), and other factors such as hydrology, land management, and atmospheric carbon dioxide concentration (Clark *et al.*, 2010). Rising DOC concentrations have implications for human health, as harmful by-products can be formed when DOC is chlorinated during water treatment (Chow *et al.*, 2003). Additionally, high levels of DOC result in increased water treatment costs due to the use of a higher coagulant dose, increased filter backwashing, and the production of larger amounts of sludge (McDonald *et al.*, 1991). DOC cycling is also of interest to those studying carbon budgets, and significantly affects aquatic ecosystem functioning via its influence on light penetration, mobility and form of toxic substances, and the supply of energy and nutrients.

DOC is typically measured by high temperature combustion using infra-red detection either as 'non-purgeable' organic carbon (i.e. that part of the total dissolved carbon that is not removed following acidification of the sample and sparging with oxygen gas), or by calculating and then subtracting inorganic carbon from total carbon. These methods are expensive and time-consuming, and require access to specialist analytical equipment. A second method is to use absorbance at certain wavelengths in the ultraviolet-visible (UV-vis) range as a proxy for DOC. Wavelengths used include 254 nm (e.g. Edzwald, 1985), 330 nm (e.g. Moore, 1987), 360 nm (e.g. Collier, 1987) and 400 nm (e.g. Gibson *et al.*, 2009). Routinely, a calibration curve is established between the chosen wavelength and a limited series of DOC measurements, so that further DOC concentrations can be calculated from the calibration. Wallage and Holden (2010) demonstrate that caution must be used when using absorbance as a proxy for DOC, as relationships between DOC and absorbance change over

time, with depth, and with management practices. Tipping *et al.* (2009) created a DOC model for non-polluted waters, using absorption at 254 nm and 340 nm, but Grayson & Holden (2012) argued that wavelengths under 300 nm are unsuitable as DOC proxies, as they display rapid fluctuations in absorbance and a lack of differentiation between wavelengths. However, wavelengths in the 400 nm region can sometimes be unsuitable as iron can interfere with absorbance readings (Kritzberg & Ekström, 2012). Other colorimetric methods exist to measure DOC, whereby the chemically-induced colour change of a sample is measured with a spectrophotometer, such as that proposed by Bartlett & Ross (1988). Finally, fluorescence spectroscopy can be used as a method to characterise DOC. This approach is valuable due to its high specificity and sensitivity (Chen *et al.,* 2003). An alternative method, rather than UV-vis, may therefore prove useful as a surrogate DOC measure.

One feature of waters draining from wetlands, including peatlands, is the presence of recalcitrant phenolics (Wetzel, 1992), which are secondary plant metabolites (Hättenschwiler & Vitousek, 2000). Their concentrations vary seasonally (Kaiser *et al.,* 2001) and are controlled by plant characteristics (Wetzel, 1992), and physical and chemical factors such as photodegradation (Faust & Holgne, 1987). They accumulate due to a lack of oxygen in waterlogged soils, which limits the activity of the extracellular enzyme phenol oxidase (Freeman *et al.,* 2004). Phenolics are part of the coloured component of DOC (Toberman *et al.,* 2008). They are aromatic, but DOC also includes aliphatic compounds (Leenheer & Croué, 2003). Relationships between DOC and phenolics have been noted previously (Kang *et al.,* 2002, Hagedorn & Machwitz, 2007). The aim of this analysis is therefore to determine if an empirical relationship exists between the concentrations of DOC and phenolic-OH (hydroxyl group) in upland waters, and under what conditions such a relationship might exist: whether it is the same for different sites, soils and samples types, and how stable it is in the long term. Based on the results of this analysis, the potential for using phenolics as a surrogate measure for DOC is critically evaluated.

2.2. Materials and Methods

2.2.1. Study Sites

A total of 2020 water samples were taken from eight sites in northern Wales and northern England, UK, summarised in table 1. At Ffynnon Eidda 192 samples were from ditch water and 132 samples were from pore water. The Migneint site was split into three sub-sites: pore waters from two different soil types (blanket peats and peaty podzols) and soil

leachate samples. The Peaknaze site was split into two sub-sites (again with pore water samples from blanket peat and peaty podzols). For each peat and podzol sub-site approximately 600 data points were available, but random selections of 300 were taken so as not to bias the model towards these sites. Other samples were taken from either standing water bodies or pore water (using piezometers or Rhizon samplers at 10 cm depth), or were generated from soil samples (from 10 cm or 30 cm depth) in the laboratory (leachate). At all sites, sampling was repeated at fixed locations on a number of occasions.

Table 1. Location of field sites (ordered by sample type), including soil type, sample type, and the time period over which sampling took place. For pore waters, P indicates a piezometer sampler, and R indicates a Rhizon sampler. The fen mesocosms consisted of rafts of vegetation floating in individual pools.

Site	Lat	Lon	Soil Type	Sample Type	No. Samples	Altitude (m)	Sampling dates
Ffynnon Eidda	52.97N	3.84W	Peat	Ditch/Pore (P)	326	490	Oct 2010 - Nov 2011
Migneint	52.99N	3.82W	Peat	Pore (R)	300	450	Aug 2007 - Jan 2012
Migneint	52.99N	3.81W	Podzol	Pore (R)	300	480	Sept 2007 - Jan 2012
Peaknaze	53.47N	1.91W	Peat	Pore (R)	300	440	Aug 2007 - Jan 2012
Peaknaze	53.47N	1.91W	Podzol	Pore (R)	300	430	Aug 2007 - Jan 2012
Plynlimon	52.46N	3.74W	Peat	Pore (R)	167	530	May 1992 – Sept 1992
Migneint	52.99N	3.82W	Peat	Leachate	45	450	Sept 2011, Jan 2012
Fen Mesocosms	53.22N	4.13W	Peat	Pool	210	20	June 2011 - July 2011
Llyn Cwellyn	53.07N	4.15W	Peat/Loam	Lake	24	140	Nov 2009 - Oct 2011
Llyn Conwy	52.99N	3.82W	Peat	Lake	24	450	Nov 2009 - Oct 2011
Llyn Teyrn	53.07N	4.03W	Peat	Lake	24	370	Nov 2009 - Oct 2011

2.2.2. Phenolics Assay

Water samples were filtered through Whatman 0.45 μm cellulose nitrate filters, and phenolic concentrations were determined using a method adapted from Box (1983). 0.25 ml of sample was added to a clear microplate well. 12.5 μl of Folin-Ciocalteau reagent was added (using a pipette calibrated to 1.98% accuracy with a covariance of imprecision of 0.57%), followed by 37.5 μl of Na_2CO_3 (200 g L^{-1}). After 1.5 hours the absorbance was measured at 750nm on a BMG Fluostar Galaxy or Molecular Devices M2e Spectramax plate-reader. Phenolic concentrations were then derived from the preparation of a standard curve using laboratory-prepared standards of known concentration (0, 1, 2, 4, 6, 8, 10, 15, 20 mg L^{-1}). Additional standards (0.2, 0.5, 0.75, 1.5 mg L^{-1}) were used for the analysis of samples from Llyn Cwellyn, Llyn Conwy and Llyn Teyrn as phenolic concentrations from these sites were frequently found to be < 1 mg L^{-1}. Box (1983) cited a limit of detection of 6 μg phenol

L^{-1} and a standard deviation of 4.1% at 1 mg phenol L^{-1} for this assay, although more recently the limit of detection has been cited as 25 μg L^{-1} (Thoss *et al.*, 2002).

2.2.3. DOC Analysis

All samples were filtered through Whatman 0.45 μm cellulose nitrate filters and analysed using an Analytical Sciences Thermalox Total Carbon analyser. Samples were acidified (pH < 3) and sparged with oxygen to remove any inorganic carbon, and DOC concentrations calculated using a seven point calibration curve (plus a quality control sample), with additional standards to check for drift, and several samples (1-3 per run) duplicated to check for reproducibility. Each individual sample was injected 5 times, and the result accepted if the coefficient of variation of the five injections was less than 3%.

Plynlimon samples were analysed differently. They were diluted with sulphuric acid and purged with oxygen (to remove inorganic carbon), after which a digestion reagent (consisting of 0.044 M $K_2S_2O_8$, 0.089 M $Na_2B_4O_7$ and H_2O) was added. Following exposure to a UV source, radicals react with the organic material in the sample, which is converted into CO_2 and H_2O. By gas dialysis the CO_2 is lead into a colour reagent. Colour intensity (measured at 550 nm) then decreases proportionally to the change in pH caused by the CO_2, and this decrease is in relation to the DOC.

2.2.4. UV-vis analysis

UV-vis analysis was conducted on 192 samples from the Ffynnon Eidda site using a Molecular Devices M2e Spectramax plate-reader. Light absorbance at the 254 nm and 400 nm wavelengths was measured.

2.2.5. Statistics

Phenolic and DOC values were paired together in order to examine any relationship between them, and statistical analysis carried out using SPSS v16.0.1 (IBM Corporation, http://www-01.ibm.com/software/analytics/spss/products/statistics/). Different sites and samples were compared using t-tests and ANOVAs or, where data were not normally distributed (identified by Kolmogorov-Smirnov Test), Mann-Whitney and Kruskal Wallis tests, with Bonferroni-adjusted p values. The Bonferroni correction is a method to control the familywise error rate, but does increase the probability of missing real differences in the data.

2.3. Results

2.3.1 General model

The linear regression gave the fit shown in Figure 1.

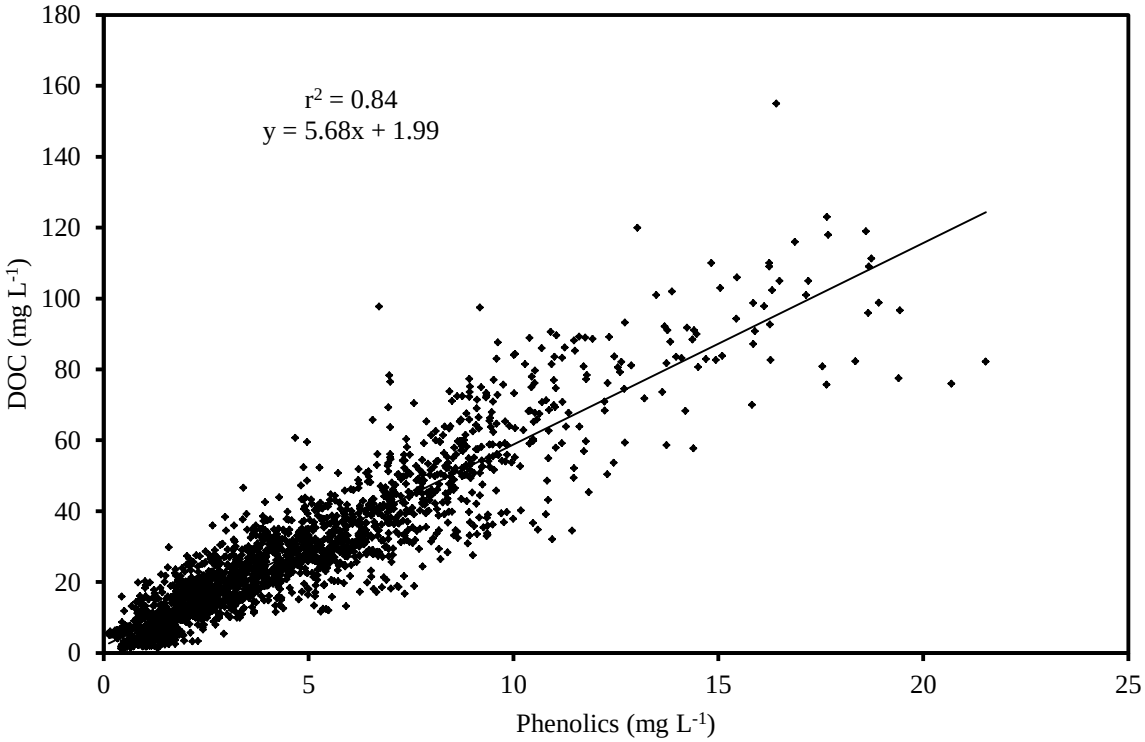

Figure 1. Observed relationship between phenolic concentrations (mg L^{-1}) and DOC concentrations (mg L^{-1}) for all 2020 water samples. $r^2 = 0.84$, residual variance = 72.051, $p < 0.001$.

This linear regression allowed DOC concentrations to be calculated directly from phenolic concentrations, according to the formula:

$$DOC = (5.68 \times Phenolics) + 1.99 \qquad (1)$$

where DOC is calculated in mg L^{-1}, and Phenolics is the measured phenolic concentration, also in mg L^{-1}. Standard errors of the model parameters are respectively (5.68) $^{+}$/- 0.06 and (1.99) $^{+}$/- 0.32. Confidence intervals at 95% were 2.24 (lower) and 2.33 (upper).

This general model was then tested using phenolic and DOC data from other sites in north Wales (figure 2). These were stream samples from the Nant y Brwyn (an upland stream in a peat catchment, 410 m ASL), leachate samples from Alwen Reservoir (an upland forested peat catchment, 390 m ASL), and pore water samples from Llyn Serw (an upland peat catchment, 460 m ASL). Fits were generally good ($R^2 \geq 0.75$) although the model tended to overestimate DOC concentrations at the Nant y Brwyn and underestimate them at Alwen Reservoir and Llyn Serw. The model calculated DOC to a mean accuracy of 86%

(modelled values were on average 1.69 mg L^{-1} different to measured, standard error 0.32 mg L^{-1}) at the Nant y Brwyn, 81% (mean difference of 2.21 mg L^{-1}, SE = 0.36 mg L^{-1}) at Alwen Reservoir, and 86% (mean difference of 7.65 mg L^{-1}, SE = 0.94 mg L^{-1}) at Llyn Serw.

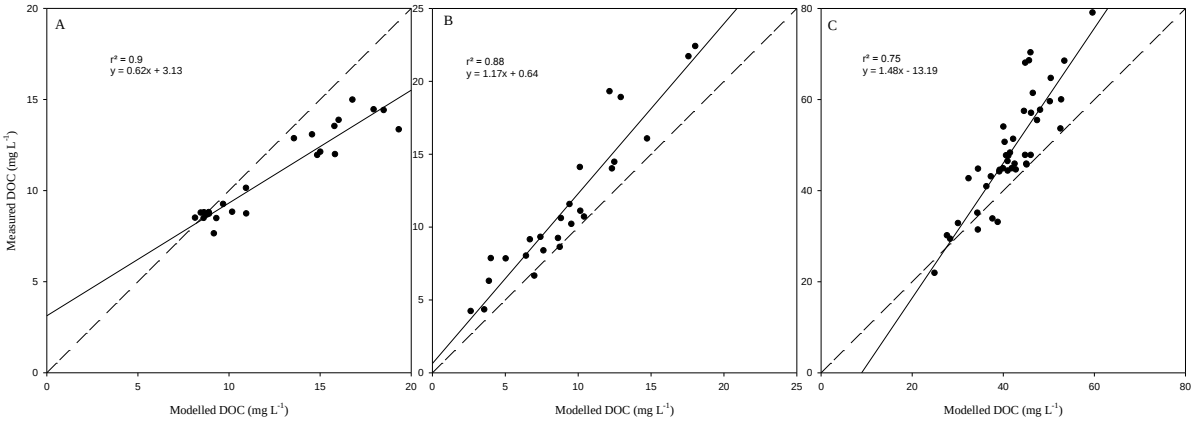

Figure 2. Regression between measured DOC and modelled DOC (mg L^{-1}) in Nant y Brwyn stream water, *n*=24, r^2=0.90 (A), Alwen Reservoir leachate samples, *n*=25, r^2=0.88 (B), and Llyn Serw pore water samples, *n*=44, r^2=0.75 (C). p<0.001 for each relationship. Dashed line shows 1:1 relationship.

Despite the strength of the model, there was variation in the relationship between DOC and phenolics at the different sites. Figure 3 shows the median ratio of phenolic to DOC concentrations at each site, which ranged from 0.14 : 1 to 0.27 : 1. Differences in the ratios were tested using the Kruskal Wallis test, followed by Mann-Whitney tests with Bonferroni corrections to control the probability of false positive results. A total of 26 tests were performed (table 2). The highest mean phenolic:DOC was found at Llyn Teyrn but there is no significant difference when compared to the other two lakes Llyn Cwellyn and Llyn Conwy. The lowest mean phenolic:DOC was in the Peaknaze podzol and the fen mesocosms. It can be noted that spatial proximity of sampling sites is sometimes, but not always, associated with a similar response between DOC and phenolics. For instance, the peat and podzol sub-sites at Peaknaze are approximately 200 m apart and have no significant difference in their ratios. However, the Migneint peat and podzol pore water sample sites which are 500 m apart do show a significant difference.

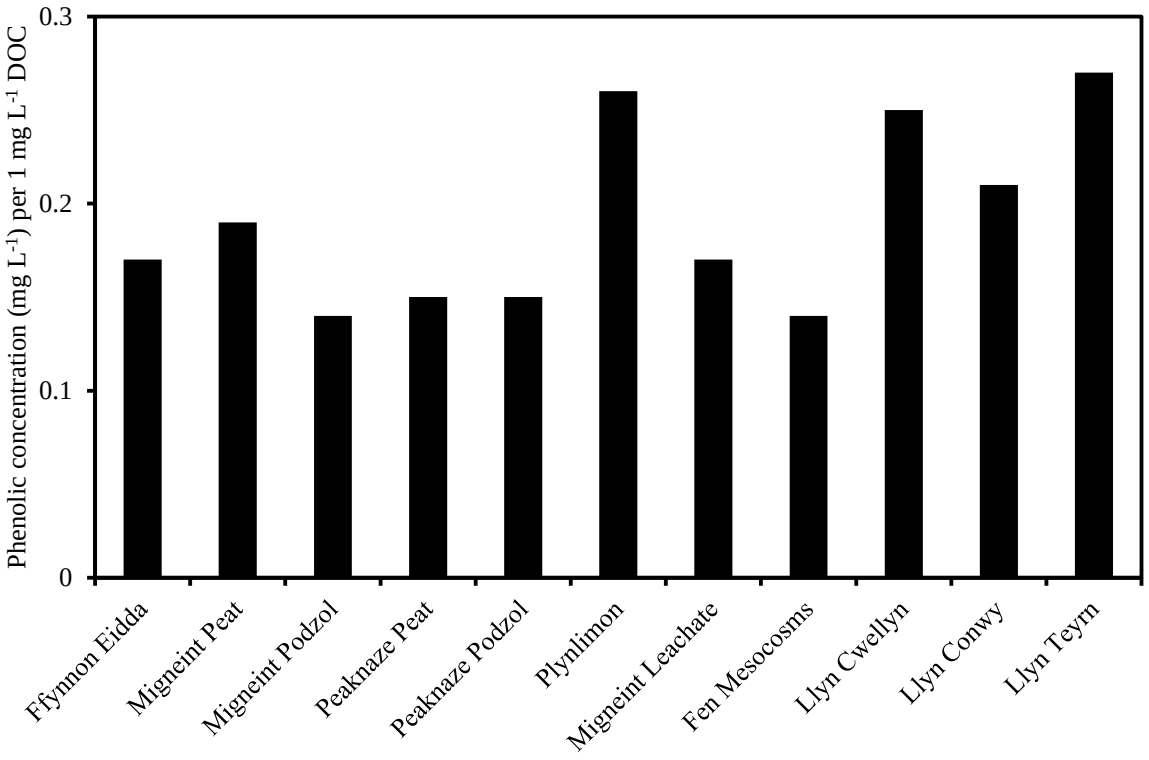

Figure 3. Median phenolic concentrations (mg L^{-1}) per 1 mg L^{-1} DOC concentrations for each site used in the model. Table 2 shows where significant differences are found.

Table 2. Results of Mann Whitney tests to compare for site differences in the median ratio of phenolics to DOC. Asterisks indicate a significant difference at a Bonferroni corrected p value <0.05. NS indicates no significant difference. A blank space shows where no comparison was carried out. It is unfeasible to run all possible pairwise comparisons as the Bonferroni correction would then produce a critical value of significance that is too restrictive. Sites along the top are abbreviated, but are in the same order as those down the side.

	Ppe	Mpod	Ppod	Mle	Lcw	Lco	Lt	Fe	Fen	Plyn
Migneint Peat	*	*	*	NS	*	NS	*	*	*	*
Peaknaze Peat		NS	NS					*		*
Migneint Pod			NS	NS		*		*		
Peaknaze Pod										
Migneint Leach								NS		
Llyn Cwellyn						NS	NS		*	
Llyn Conwy							NS		*	
Llyn Teyrn									*	
Ffynnon Eidda										*
Fen Mesocosms										
Plynlimon										

A further investigation of different samples types is useful. For instance, there is no significant difference between the two podzol soils at Peaknaze and the Migneint. Figure 4 displays this amalgamated podzol data against its peat equivalent. The mean ratio of phenolics to DOC is significantly different between the two soil types: 0.15 : 1 in the podzol, and 0.18 : 1 in the peat. Additionally, the concentrations of DOC and phenolics cover a larger range and increase to higher values in the peat soil. Phenolic concentrations had a range of 21.05 mg L^{-1} with a maximum of 21.53 mg L^{-1} in the two peat soils, compared with a range of 15.83 mg L^{-1} and maximum of 16.27 mg L^{-1} in the podzols. There is also a difference between surface water and pore water when all sites are considered (figure 5). The mean proportion of phenolics to DOC is 0.20 : 1 in pore water compared to 0.17 : 1 in surface water. The three lakes all possessed a high proportion of phenolics but their relatively small sample sizes compared to other surface waters reduced their influence on the mean. Concentrations of phenolics and DOC ranged more in the pore water and reached higher levels. Maximum pore water phenolic concentration was 21.53 mg L^{-1}, whilst the highest surface water value was 12.71 mg L^{-1}.

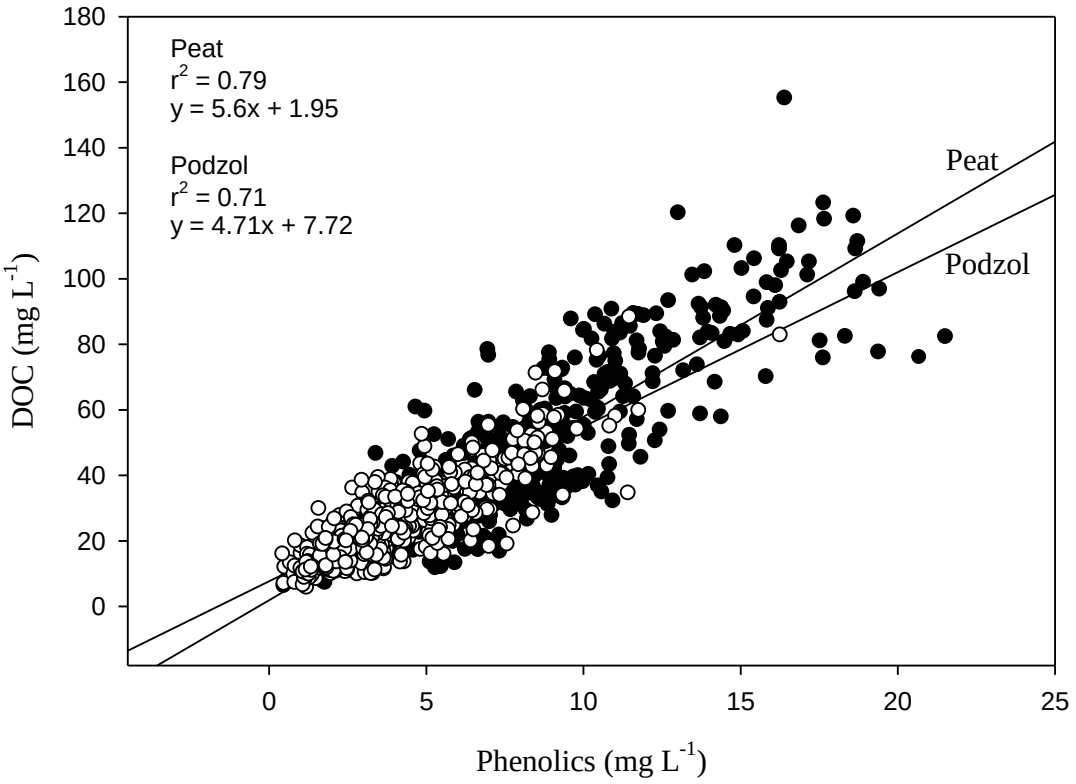

Figure 4. Regression between phenolic and DOC concentrations (mg L^{-1}) for the Migneint and Peaknaze podzol (white circles) and peat (black circles) sites. *n*=600 for each soil type. Podzol r^2=0.71. Peat r^2=0.79. For both soils $p<0.001$.

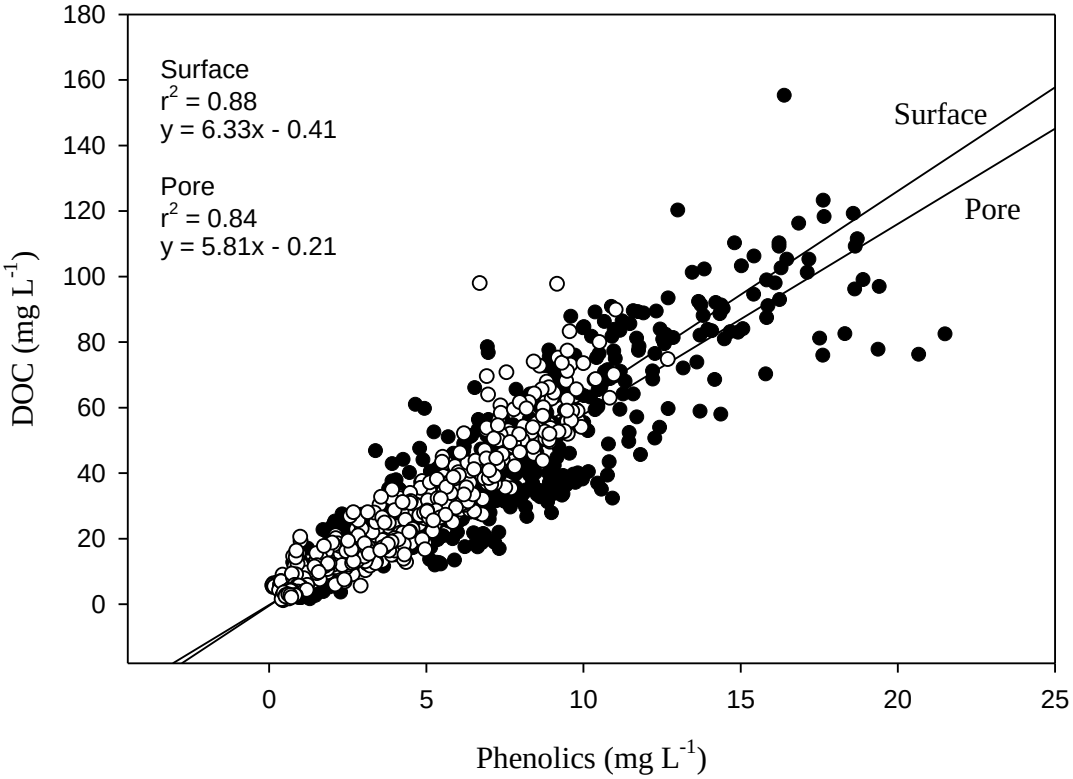

Figure 5. Regression between phenolic and DOC concentrations (mg L^{-1}) for surface waters (white circles - from Ffynnon Eidda, Llyn Cwellyn, Llyn Conwy, Llyn Teyrn, and fen mesocosms – *n*=608) and pore waters (black circles - from Migneint peat, Migneint podzol, Peaknaze peat, Peaknaze podzol, and Plynlimon – *n*=767). Surface waters r^2=0.88. Pore waters r^2=0.84. For both samples types $p<0.001$.

As phenolic concentrations are affected by factors such as vegetation growth, microbial processes and phenol oxidase activity (Freeman *et al.*, 2001b), their concentrations vary seasonally. Figure 6 details these variations for a time period of just over four years. Although not always consistent, there are occasions when all four sites respond similarly; this is perhaps most pronounced in March 2011 when all sites show a large spike, with a lesser peak following in July/August 2011. There are also occasions where just two sites respond simultaneously, such as peaks for both Migneint sites during October 2009. There is extensive interannual variation, however, with peaks and troughs in the relationship occurring at different times during different years.

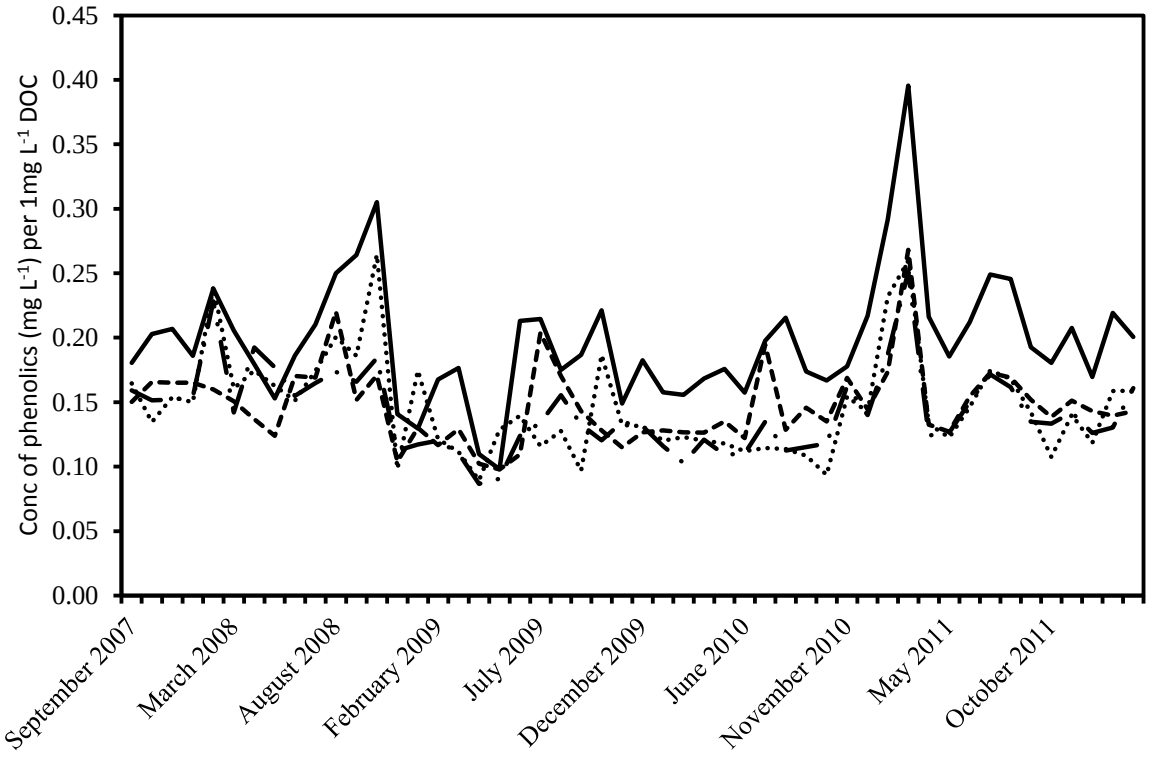

Figure 6. Changes in the mean proportion of phenolics to DOC for four sites from September 2007 to January 2012, with an approximate monthly sampling frequency. Sites are: Migneint peat – solid line, Migneint podzol – dotted line, Peaknaze peat – dashed line, Peaknaze podzol – dotted/dashed line. For each site and each date the mean is generated from *n*=12.

2.3.2 Site-specific model and comparison with UV-vis method

Results indicate: 1) that the general model calculated DOC to a mean accuracy of 81-86%; 2) that there was considerable difference between sites and soils in the mean ratio of phenolics to DOC. Therefore we investigated the possibility of using phenolic measurements as a proxy for DOC on a specific site basis, with the hope of improving the accuracy and giving more appropriate modelled DOC values. To investigate this a random selection of 100 paired phenolic and DOC measurements were selected from surface water samples from the Ffynnon Eidda site, and a regression fitted to give the site-specific equation (r^2=0.87, $p<0.001$) :

$$DOC = (5.83 \times Phenolics) - 0.59 \qquad (2)$$

where DOC and phenolics are calculated in mg L^{-1}. Equation 2 was then applied to the remaining 92 surface water phenolic measurements from Ffynnon Eidda to calculate DOC, as was equation 1. Equation 1 (the model using data from all sites) calculated DOC to a mean accuracy of 83.67% (standard error = 1.96%) whilst equation 2 (site-specific model) gave a

mean accuracy of 86.54% (SE = 1.57%). A paired t-test (after the data was normalised by subtracting each value from 100% followed by square root transformation) showed this difference to be significant ($p<0.05$).

We also compared a site-specific phenolics model against a colour-carbon model: that is, a regression of DOC concentration against light absorbance at a certain wavelength. For this, 192 data points from the Ffynnon Eidda surface water dataset were used, and phenolic concentrations compared against absorbance at 254 nm and 400 nm (figure 7). Absorbance at 254 nm gave the best fit, closely followed by phenolic concentration, whilst absorbance at 400 nm gave the weakest fit.

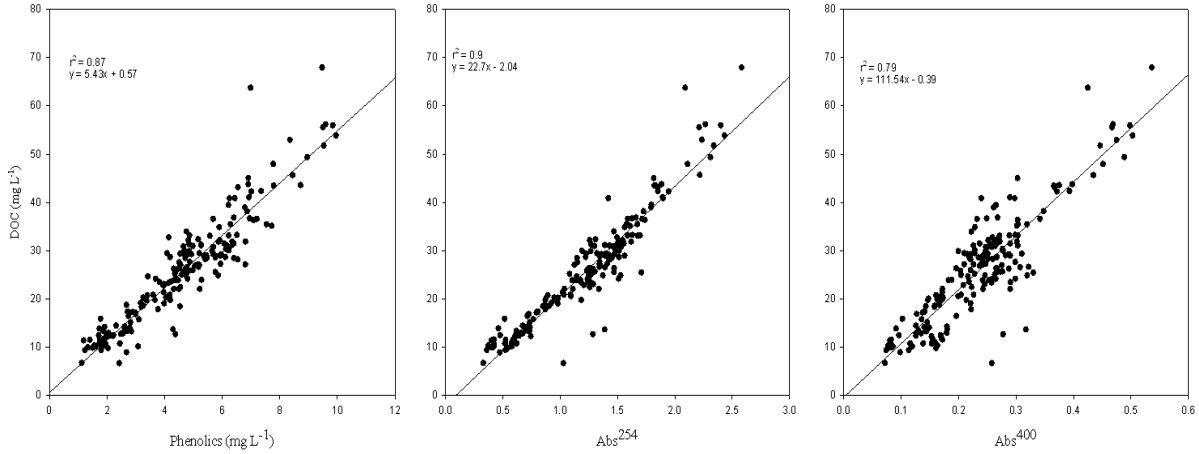

Figure 7. Regressions of DOC concentration against A) phenolic concentration, B) absorbance at 254 nm, C) absorbance at 400 nm, for 192 ditch water samples from Ffynnon Eidda. r^2 values A) 0.87, B) 0.9, C) 0.79. For all regressions $p<0.001$.

Finally, if phenolic concentration is to be used as a proxy for DOC it is useful to know if a calibration can be established using a small number of measurements, and how this compares to a colour-carbon calibration. To test this a random sub-sample of 25 measurements was taken from the Ffynnon Eidda data-set and analysed by regression; r^2 and regression equation were noted – to allow a simple comparison the regression was forced through the origin. This method was repeated twenty times for DOC and phenolics, DOC and absorbance at 400 nm, and DOC and absorbance at 254 nm. The mean r^2 values were 0.83 for the phenolics model, 0.71 for the 400 nm model, and 0.85 for the 254 nm model. ANOVA revealed that there was no significant difference in the mean r^2 between the phenolic and 254 nm model, but that the 400 nm model differed significantly from both ($p<0.001$). The mean slope of all twenty regression equations was then compared against the slope of the regression that used all 192 data points; this gives a measure of the magnitude of error that using a small calibration brings. The mean slope difference was 2.65% for the

phenolic model, 5.59% for the 400 nm model, and 3.16% for the 254 nm model. The only significant difference was between the phenolic model and the 400 nm model ($p<0.05$).

2.3.3 Phenolic degradation in stored samples

To investigate how phenolics degrade in stored water samples a small number of samples from the Ffynnon Eidda site were reanalysed for phenolic concentrations. One set of samples had been in storage for 13 months whilst the second set had been stored for 8 months. They had been stored in plastic Nalgene® bottles (Thermo Scientific) in the dark at 4^{o}C. The site-specific model was then applied to phenolic concentrations that had been measured both before and after storage (table 3). The mean loss of phenolics during storage was 0.74 mg L^{-1} (11.7%) for the 8 month samples and 0.58 mg L^{-1} (8.3%) for the 13 month samples. The smaller value for the 13 month samples is due to the fact that phenolic concentration increased in two samples. Removing these numbers gave a mean of 0.77 mg L^{-1} (12.9%). After 8 months in storage the phenolic measurements calculated DOC, on average, to within a mean of 2.77 mg L^{-1} or 91.4% (compared to 1.87 mg L^{-1} or 93.9% before storage). After 13 months DOC could be calculated to 5.29 mg L^{-1} or 84.6% (compared to 3.43 mg L^{-1} or 89.3% before storage). Additional analysis of pore water samples from Ffynnon Eidda revealed that after 8 months the mean loss of phenolics was 0.92 mg L^{-1} (12.4%), but after 13 months there was a mean increase of 0.62 mg L^{-1} (9.4%) (table 4).

Table 3. The extent of phenolic degradation in stored water samples taken from ditch water at Ffynnon Eidda. 'Phenolics' is the concentration taken immediately after sampling. 'Phenolics^{8}' or 'Phenolics^{13}' is the concentration of the same sample after either 8 or 13 months of storage in the dark at 4^{o}C in plastic Nalgene® bottles. 'Phenolics^{diff}' is the concentration change following storage, - indicates a loss, +indicates a gain. 'Meas DOC' is the measured DOC concentration. 'Mod DOC' is the estimate DOC concentration using the site-specific model, calculated using the original phenolic measurement. 'Mod DOC^{8}' and 'Mod DOC^{13}' are the estimated DOC concentrations using the site-specific model, calculated using the phenolic measurements after either 8 or 13 months of storage. All concentrations are in mg L^{-1}.

Sample	Phenolics	Phenolics^{8}	Phenolics^{diff}	Meas DOC	Mod DOC	Mod DOC^{8}
1	6.13	5.61	-0.52	30.3	32.8	30.2
2	4.99	4.94	-0.05	25.9	27.1	26.8
3	5.76	5.34	-0.43	28.9	31.0	28.8
4	5.71	5.06	-0.65	30.7	30.7	27.4
5	6.41	5.32	-1.09	31.4	34.2	28.7
6	6.35	5.19	-1.17	31.1	33.9	28.1
7	5.66	4.90	-0.76	29.9	30.4	26.6
8	7.09	5.85	-1.24	36.3	37.7	31.4
9	5.97	5.41	-0.56	29.2	32.0	29.2
10	6.52	4.94	-1.58	33.2	34.8	26.8
11	6.30	5.53	-0.77	35.4	33.7	29.8
12	4.77	4.75	-0.02	28.9	26.0	25.9
Sample	Phenolics	Phenolics^{13}	Phenolics^{diff}	Meas DOC	Mod DOC	Mod DOC^{13}
13	6.92	5.54	-1.38	45	36.8	29.8
14	5.21	4.84	-0.37	29.4	28.2	26.3
15	5.46	4.96	-0.50	29	29.4	26.9
16	1.93	2.26	+0.33	14.1	11.6	13.3
17	5.92	5.23	-0.68	32.1	31.7	28.3
18	4.66	5.04	+0.37	30.8	25.4	27.3
19	4.87	4.79	-0.08	33.1	26.5	26.1
20	7.02	6.03	-0.98	42.2	37.3	32.3
21	5.88	5.15	-0.73	31.8	31.5	27.9
22	7.72	5.65	-2.07	35.1	40.8	30.4
23	6.23	5.38	-0.86	33.1	33.3	29.0
24	3.43	3.41	-0.02	24.6	19.2	19.1

Table 4. The extent of phenolic degradation in stored water samples taken from pore water at Ffynnon Eidda. 'Phenolics' is the concentration taken immediately after sampling. 'Phenolics^{8}' or 'Phenolics^{13}' is the concentration of the same sample after either 8 or 13 months of storage in the dark at 4^{o}C in plastic Nalgene® bottles. 'Phenolics^{diff}' is the concentration change following storage, - indicates a loss, +indicates a gain. All concentrations are in mg L^{-1}.

Sample	Phenolics	Phenolics^{8}	Phenolics^{diff}
1	5.39	4.53	-0.85
2	7.20	6.39	-0.81
3	8.00	7.22	-0.78
4	6.88	6.52	-0.36
5	6.94	6.61	-0.32
6	5.66	5.14	-0.52
7	9.23	6.71	-2.52
8	7.25	6.85	-0.40
9	7.03	5.41	-1.62
10	8.43	6.36	-2.07
11	8.94	8.55	-0.39
12	5.48	5.05	-0.43
Sample	Phenolics	Phenolics^{13}	Phenolics^{diff}
13	5.54	6.45	+0.90
14	7.40	7.11	-0.29
15	6.10	6.52	+0.42
16	9.61	10.10	+0.49
17	7.57	7.31	-0.26
18	6.72	7.93	+1.21
19	6.95	8.82	+1.87

2.4. Discussion

2.4.1. Using the general phenolic model to calculate DOC

This analysis shows that phenolic concentrations can be used to give an estimate of DOC concentrations for the pore waters and drainage waters of peaty soils. A general model using data from numerous sites allowed DOC to be calculated for three new sites at a mean accuracy of 81-86%; these three sites included pore water, surface water, and leachate samples. For each of the three sites, there was some evidence of small systematic errors in DOC predictions, due to site-specific variations in the ratio of phenolics to DOC, relative to the whole-dataset mean. One of the reasons for the high phenolic concentrations typically

observed in wetlands and uplands seems to be due to the occurrence of certain plant species. *Sphagnum* species, *Vaccinium myrtillus*, *Calluna vulgaris*, *Empetrum hermaphroditum*, and *Erica australis* are all phenolic-rich species (Rudolph & Samland, 1985, Gallet & Lebreton, 1995, Kähkönen *et al.*, 1999, Castells, 2008, Carballeria, 1980) and are typical of upland bog vegetation. High water levels that maintain anaerobic conditions constrain phenol oxidase activity and prevent the decomposition of phenolics, causing waters drained from these areas to have high phenolic concentrations (Freeman *et al.*, 2004). Variations in factors such as water table, temperature, soil type and vegetation may therefore explain some of the variability in the relationship between sites. For instance, the Migneint podzol site displays very low concentrations of phenolics per unit of DOC compared to the nearby Migneint peat site and this could be attributed to vegetation; the podzol site is typified by *Festuca ovina* and *Juncus squarrosus* and lacks the *Calluna* species that dominate the peat site. There is therefore less potential for the vegetation to release high concentrations of phenolics. In addition, it is a well drained soil so phenol oxidase activities will be higher, resulting in higher rates of phenolic degradation (Freeman *et al.*, 2001b).

A full understanding of site differences is complex, however. Despite the Migneint peat and podzol sites showing differences in the phenolic to DOC ratio, the adjacent Peaknaze peat and podzol sites do not. Like the Migneint sites, the peat site is predominantly comprised of *Calluna* and other bog species, whilst the podzol site largely features *Festuca ovina*, although *Calluna* is present. It therefore seems likely that the presence of *Calluna* could account for the lack of an observed difference at Peaknaze. Alternatively, it is possible that other environmental factors are the primary controller of phenolic concentrations at Peaknaze, such as shared precipitation and temperature. The long-term data sets from the paired Peaknaze and Migneint sites clearly show shared changes in the phenolic to DOC ratio. Some of these will be due to large scale weather events; a severe drought across the UK could stimulate phenol oxidase activity at all sites, thus causing an associated decline in phenolic concentrations. Drought conditions have also been shown to enhance both the abundance and diversity of bacteria that are capable of degrading phenolic compounds (Fenner *et al.*, 2005). On a similar theme, a localised mountain storm on the Migneint would be observed as a spike in the phenolic to DOC ratio as phenol oxidase is suppressed due to anaerobic conditions facilitating the accumulation of phenolics (Freeman *et al.*, 2004). Where only one of the four locations shows a change this must be attributable to localised factors, such as vegetation controls.

There was no significant difference in the ratio of phenolics to DOC in the three lakes (Llyn Teyrn, Llyn Cwellyn and Llyn Conwy), and they all showed relatively high proportions of phenolics. This can partly be explained by the fact that all three are humic lakes; Shimp and Pfaender (1985) showed that when microbial communities become adapted to increased levels of humic acids, their capability to degrade phenolics is reduced. Processing of fresh DOC can occur rapidly in lakes (Tranvik *et al.,* 2009) and, coupled with the high dilution effect, differences in phenolic:DOC are unlikely to be observed on the same magnitude as those occurring in soils. Phenolic concentrations and the other fractions of lake DOC will vary throughout the year, due to changing hydrological conditions (Sachse *et al.,* 2001), and differences in the efficiency of photolysis and microbial degradation (Hwang *et al.,* 1986).

Leachate samples from the Migneint were not significantly different from pore water samples from the Migneint peat site but the phenolic content of the leachate samples varied by an order of magnitude; the lowest concentration of phenolics to 1 mg L^{-1} of DOC was 0.07 mg L^{-1}, whilst the highest was 0.72 mg L^{-1}. Other work from forest ecosystems has demonstrated that one of the main components of fresh leachate is phenolics (Yavitt & Fahey, 1986, Beggs & Summers, 2011) so it seems likely that these differences are driven by the depth of samples from the soil profile, and the availability of phenolics from adjacent vegetation. A comparison of sample types revealed that the ratio of phenolics to DOC was higher in pore water than surface water, and it can be hypothesised that this is due to the increased leaching of phenolics into pore water from fresh litter (Beggs & Summer, 2011). Additionally, precipitation will contribute to surface water, and organic carbon in rainfall has been shown to consist of <1% phenolics (Likens, 1983).

Taken together these findings suggest that a general model can be used to calculate DOC, but that variations in sample type, soil type, vegetation, and climate will all contribute a degree of error. Therefore the general model should be a 'last resort' for situations where a site-specific calibration isn't possible. For instance, Worrall *et al.* (2012) applied a general colour-carbon calibration to sites where a site-specific calibration was unavailable. For similar cases, the general phenolics model can be used to provide an additional estimate of DOC concentrations.

2.4.2. Using a site-specific model to calculate DOC

Considering the uncertainty that environmental and climatic factors induce in a general model, it is unsurprising that a site-specific regression of phenolics and DOC at Ffynnon Eidda gave a stronger fit and was significantly more accurate. The exact accuracy

of any site-specific model will depend on the extent of phenolic variation throughout the year, which will be controlled by the aforementioned external factors. To generate a robust model, sampling should take place at different times throughout the year (assuming the model will be used to calculate DOC for an annual data series) and under different climatic conditions. This should allow an 'average' model to be produced, rather than one that systematically over- or underestimates DOC.

2.4.3. Comparison of phenolic-based and absorbance-based DOC estimation

A comparison of the performance of the site-specific phenol model to colour-carbon models indicated that a model based on absorbance at 254 nm produced a slightly better calibration than using phenolics, but that a model based on 400 nm model was not as strong as either. It should be noted that none produced fits that were as good as those produced by Tipping *et al.,* (2009) using a two wavelength (254 nm and 340 nm) model, but this method was not directly investigated here.

The models were all created using a large number (192) of data points. A useful model would, in reality, be constructed from as few data points as possible to save on the costs of directly measuring DOC. Repeatedly generating models for each proxy (phenolics, 254 nm, 400 nm) using just twenty five randomly selected data points showed that the 254 nm model was the strongest on average, with the phenolics model only slightly weaker. Again, the 400 nm model was considerably weaker compared to the other two. However, the phenolic model was the most accurate; on average the twenty five point regression only deviated from the full (192 point) model by 2.65%. This was significantly better than the 400 nm model (5.59%) but showed no difference to the 254 nm model (3.16%).

These results therefore suggest that a small-dataset, site-specific calibration of phenolics to DOC can be as or more accurate than a colour-carbon calibration, depending on the wavelength of light absorbance used. Accuracy will vary throughout the year as phenolic concentrations fluctuate, but the same problem is true of colour-carbon calibrations, as these also vary seasonally (Watts *et al.*, 2001, Wallage & Holden, 2010). Additionally, this study shows that a colour-carbon calibration at 254 nm is more accurate than one using 400 nm as a proxy, at least for the site examined. Part of the reason for this could be iron interference, as iron can contribute to absorbance measurements at approximately 400 nm (Kritzberg & Ekström, 2012). Wilson *et al.* (2011) found that the best proxy for DOC concentrations from different catchments on blanket bog was either absorbance at 254 nm or 400 nm. The results presented here suggest that studies using colour-carbon calibrations should investigate the

potential of both wavelengths, as many just use 400 nm (e.g. Gibson *et al.*, 2009, Wallage & Holden, 2010, Rowson *et al.*, 2010).

UV-vis scanning of water samples for these models must take place within a week of sampling to ensure accuracy, and it is often desirable to analyse samples within a day of collection (e.g. Wilson *et al.*, 2011), but phenolics are relatively stable to microbial degradation (Chian, 1977) and thus samples do not have to be assayed immediately. There is a lack of information in the literature concerning the exact time samples can be stored for, but Afghan *et al.* (1974) noted no apparent loss after 16 days, provided samples were stored in glass bottles. However, our results demonstrate only a small loss of phenolics from plastic bottles after 8 months in storage in the dark at 4^{o}C. These samples still enabled DOC to be calculated to an acceptable degree of accuracy. Samples stored for 13 months allowed DOC to be calculated accurately, but interestingly two samples showed an increase in phenolics following storage. Theoretically this could be an analytical error, but the fact that pore water samples also showed phenolic increases after 13 months suggests it is a real effect. It may be that the increase is due to phenolic compounds leaching into the sample from the plastic bottle, but it is unknown why only some samples showed increases. More detailed work could focus on the specific rate of phenolic degradation over time which, if known, could then be incorporated into a model to allow DOC to be calculated accurately from older samples. Considering these results, however, and it can be concluded that a phenolics-based model is preferential to a UV-vis-based one if it is not feasible to analyse samples immediately. Where samples can be analysed immediately, it is likely that the two wavelength model of Tipping *et al.* (2009) will be more accurate.

2.4.4. Practical applications

If direct DOC measurements are unavailable or unaffordable then this method can be considered an effective substitute, considering: 1) the equipment needed is minimal, consisting of a few chemicals and access to a spectrophotometer able to determine absorbance at 750nm; 2) preparation time for the samples is quick; 3) a microplate can be used for the analysis, thereby allowing up to eighty four samples to be analysed at once; 4) only a small amount (0.25 ml) of sample is needed; and 5) it can be used on older samples.

Some caution may be required in extending this approach to different sample types, for example natural waters draining non-peaty soils, or leachate samples from other types of organic matter. Certain substances will also interfere with the phenolics assay; notably, iron concentrations higher than 2 mg L^{-1}. This was not considered to be an issue for the sites used

in this study; monthly samples from the Ffynnon Eidda site taken between September 2006 and September 2011 had a mean iron content of 0.86 mg L^{-1}, and only exceeded 2 mg L^{-1} on four occasions out of eighty four sampling dates (CEH unpublished data). None of the incidences of high iron concentrations coincided with high phenolic concentrations. Iron levels for a peatland stream at the Plynlimon site averaged 0.1 mg L^{-1} for the period 1990-2005, with a maximum value of 0.81 mg L^{-1} (Neal *et al.*, 2008). If iron is present in samples, then adding a centrifugation step to the method can remove the error (Box, 1983).

This model therefore seems ideal for certain situations, such as those involving practitioners and conservation agencies. For example, in the UK the incidence of drain blocking on peatlands is increasing, often under the stewardship of environmental agencies and land managers (Armstrong *et al.*, 2010). Some of these projects include monitoring of DOC, but are more often focused on other objectives such as restoration of vegetation, biodiversity enhancement and erosion control (Walker *et al.*, 2008). With limited funds and equipment for detailed scientific monitoring, it may not be possible to robustly evaluate the impacts of rewetting on water quality. The method described here offers a viable solution to gather data on the effects of rewetting on DOC, a key parameter of concern from a water supply and ecological perspective. This approach could replace or augment more commonly used colour-carbon calibrations.

2.4.5. Conclusions

Through the analysis of data from eight sites in England and Wales we show that the concentration of phenolic compounds in water samples can be used as a proxy for DOC concentration. A general model using data from all the sites allowed DOC to be calculated from phenolics at an accuracy of 81-86%. A detailed analysis at one site revealed that a site-specific calibration was more accurate than the general model, and that this compared favourably with a colour-carbon calibration. We therefore recommend this method for use where estimates of DOC concentration are needed, but where time and money are limiting factors, or as an additional method to calculate DOC alongside colour-carbon calibrations. Because tests demonstrated only small amounts of phenolic degradation over time (a loss of 0.92 mg L^{-1} after 8 months in storage) this method can be used on older samples with limited loss of accuracy.

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UV-vis spectroscopy as a proxy for dissolved organic carbon (DOC): considerations on wavelength and sample retention time

3. 1. Introduction

Dissolved organic carbon (DOC) is a component of the carbon cycle, influences the functioning of aquatic ecosystems (Karlsson *et al.,* 2009), impacts on water treatment costs (McDonald *et al.,* 1991), and has implications for human health in potable water (Chow *et al.,* 2003). Long-term increases in DOC concentrations in natural systems have been observed across the northern hemisphere (Freeman *et al.,* 2001, Stoddard *et al.,* 2003, Skjelkvåle *et al.,* 2005), with the primary driver potentially being ecosystem recovery from acid deposition (Evans *et al.,* 2012, Ekström *et al.,* 2011). Additionally, changing hydrology (Tranvik & Jansson, 2002, Worrall *et al.,* 2008), rising atmospheric carbon dioxide concentrations (Freeman *et al.,* 2004, Fenner *et al.,* 2007), drought events (Fenner & Freeman, 2011, Tang *et al.,* 2012), increasing temperatures (Freeman *et al.,* 2001) and land management strategies such as drainage and burning (Mitchell & McDonald, 1995, Holden *et al.,* 2012) have all been suggested to contribute to changes in DOC concentrations. As such, widespread monitoring of DOC concentrations takes place.

DOC can be measured directly using laboratory methods, but this requires access to specialised and expensive equipment. An alternative method is to use UV-visible (UV-vis) spectroscopy, as the absorbance of light by water from natural systems can be used as a proxy for DOC (Korshin *et al.,* 1997). In the water treatment industry, absorbance at 254 nm is often used as a surrogate for DOC because aromatic humic substances are the dominant component of DOC in natural waters, and these absorb light in the UV wavelength region (Edzwald *et al.,*1985). Humic substances can contribute up to 90% of DOC in some lakes and wetlands, although their percentage can vary considerably (Thurman, 1985). The link between aromaticity and absorbance at 254 nm has been demonstrated directly using ^{13}C NMR spectroscopy (Weishaar *et al.,* 2003). By establishing a calibration between a number of paired DOC and absorbance values, DOC concentrations can be calculated cheaply and quickly by just measuring absorbance.

Apart from 254 nm, numerous other wavelengths have been used as proxies for DOC, which table 1 lists. Occasionally DOC is calculated for a specific site using a calibration generated elsewhere (e.g. Worrall *et al.,* 2012), but Wallage & Holden (2010) caution against this, as calibrations can vary according to factors such as peat depth, land management, and

over time. However, the study in question (Wallage & Holden, 2010) investigated 400 nm as a proxy which is at the extreme upper end of the UV spectrum (and also part of the visible spectrum). As humic substances are coloured to varying degrees (Thurman, 1985) a wavelength in the visible spectrum may not be the most appropriate proxy. Measuring absorbance at a lower wavelength in the UV spectrum may produce more robust calibrations (Wang & Hsieh, 2001).

Table 1. List of wavelengths that have been used as proxies for DOC.

Wavelength (nm)	Reference
250	De Haan *et al.* 1982
254	Edzwald *et al.*,1985
260	Banoub, 1973
270	Timperley, 1985
280-400	Lawrence, 1980
300	McKnight *et al.*, 1997
320	Gorham, 1957
330	Moore, 1987a
340	Tipping *et al.*, 1988
355	Muller & Tankéré-Muller, 2012
360	Collier, 1987
365	Carpenter & Smith, 1984
400	Wallage & Holden, 2010
410	Hongve & Åkesson, 1996
420	Fosberg, 1967
436	Hongve & Åkesson, 1996
450	Hongve & Åkesson, 1996
465	Hautala *et al.*, 2000
562	Carpenter & Smith, 1984

More sophisticated methods to calculate DOC using light absorbance have been proposed, such as ones using two different wavelengths (Tipping *et al.*, 2009, Carter *et al.*, 2012), and the method of Wang & Hsieh (2001) which uses the area under the UV-vis spectra as a proxy. Despite this, numerous environmental studies continue to rely on calibrations using one wavelength (e.g. Wilson *et al.*, 2011, Muller & Tankéré-Muller, 2012). In light of this, a thorough investigation of the appropriateness of different wavelength proxies is needed, as well as a comparison of different methods.

In addition to being used as a proxy for DOC concentration, UV-vis spectroscopy is also used as a tool to provide information on the structure and composition of DOC (table 2). The E4:E6 ratio is frequently cited as a measure of humification or molecular weight (Thurman, 1985, Summers *et al.,* 1987), and is the ratio of absorbance at two wavelengths; one around 400 nm and one around 600 nm. Similarly, the E2:E3 ratio (absorbance at 250 nm and 365 nm) is used as an estimation of aromaticity and molecular weight (Peuravuori & Pihlaja, 1997), and SUVA (specific UV absorbance: an absorbance measurement, usually taken at 254 nm, divided by DOC concentration) is also a measure of aromaticity (Weishaar *et al.,* 2003). E2:E4 ratios are sometimes used, where absorbance is measured at two wavelengths; one around 200 nm and one around 400 nm. This ratio has been cited as a measure of humification (Park *et al.,* 1999), and as a comparison of the UV-absorbing functional groups and coloured ones in DOC (Selberg *et al.,* 2011, Graham *et al.,* 2012). Similarly, spectral slope ratios can provide information on molecular weight (Helms *et al*., 2008). However, doubt has been expressed over the use and applicability of some of these ratios (O'Driscoll *et al.,* 2006).

UV-vis spectroscopy is also used as a tool to investigate other, non-DOC, compounds such as organic halogen and disinfectant chlorination byproducts (Korshin *et al.,* 1996, Li *et al.,* 2000), total dissolved mercury (Dittman *et al.,* 2009), total nitrogen and nitrate (Ferree & Shannon, 2001), and in wastewater treatment (Vaillant *et al.,* 2002).

Table 2. Details of various UV-vis measures used in the investigation of DOC composition.

Measure	Wavelengths (nm)	Reference
E2:E3 ratio	250:365	Peuravuori & Pihlaja, 1997
E2:E4 ratio	252:452	Graham *et al.,* 2012
	254:436	Selberg *et al.,* 2011
	254:465	Park *et al.,* 1999
E4:E6 ratio	400:600	Moore, 1987b
	450:650	Wilson *et al.,* 2011
	460:660	Thurman, 1985
	465:665	Wallage *et al.,* 2006
SUVA	254	Weishaar *et al.,* 2003
	280	Duirk & Valentine, 2006
	400	Worrall et al., 2007

In view of the prevalence of spectrophotometric analysis, it is therefore worth considering how long a water sample can be retained in storage before analysis, and still produce an accurate and reliable result. Current practice is to measure absorbance as soon as possible after sampling, often within one day (e.g. Wilson *et al.*, 2011). Under the Disinfectant/Disinfection By-products Rule of the US Environmental Protection Agency samples for UV scanning must be analysed within two days (Karanfil *et al.*, 2002). However, there does not appear to be any detailed study in the literature describing the degradation of absorbance in stored samples over time.

The aim of this experiment is therefore four-fold: 1) to investigate the appropriateness of different wavelengths as proxies for DOC concentration, and to observe whether this changes for different sets of samples (hereafter referred to as the "DOC proxy assessment"); 2) to compare different indirect methods of DOC measurement (hereafter referred to as the "procedural comparison"; 3) to assess the suitability of the E2:E3, E2:E4 and E4:E6 ratios (hereafter referred to as the "E ratio assessment", and; 4) to repeatedly measure the weekly change (if any) in absorbance for a set of water samples (hereafter referred to as the "absorbance degradation" experiment). Taken together, the findings should ensure the best possible experimental methods for those using UV-vis spectroscopy as a tool to analyse natural waters.

3.2. Materials and Methods

3.2.1. DOC proxy assessment

In order to assess the appropriateness of different wavelengths as DOC proxies, we took water samples from two peatland sites in north Wales: the catchment of the Afon Ddu on the Migneint blanket bog (latitude 52.97°N, longitude 3.84°W), and the catchment of the Alwen Reservoir (latitude 53.07°N, longitude 3.57°W). Afon Ddu samples were from three sets: samples taken from surface water in twelve open and blocked ditches, pore water samples taken from twelve piezometers, and overland-flow (OLF) surface water samples collected from twenty four crest-stage tubes. Ditch and piezometer samples were collected monthly from July 2011 to January 2012, and OLF samples were collected for January and July 2012. Samples from the Alwen Reservoir catchment were taken monthly from six streams from October 2011 to May 2012.

Water samples were stored in the dark at 4^{o}C before analysis. Samples were filtered through Whatman 0.45 μm cellulose nitrate filters and analysed for DOC using an Analytical Sciences Ltd Thermalox Total Carbon analyser. Samples were acidified (pH < 3), sparged

with oxygen to remove any inorganic carbon, and DOC concentrations calculated using a seven point calibration curve, with additional standards to check for drift, (plus a quality control sample) and several samples (1-3 per run) duplicated to check for reproducibility. Each individual sample was injected 5 times, and the result accepted if the coefficient of variation of the five injections was less than 3%. UV-vis analysis was conducted using a Molecular Devices M2e Spectramax plate-reader. Wavelengths were scanned on a 1 nm increment from 230 nm to 800 nm, and results were corrected against blanks of ultrapure water.

Data analysis was performed using SPSS v16.0.1 (IBM Corporation, http://www-01.ibm.com/software/analytics/spss/products/statistics/). For each set of samples a regression was performed between each individual wavelength and DOC concentration, with the aim of determining which wavelength gave the highest R2 value (i.e. the strongest fit between DOC and UV-vis).

3.2.2. Procedural comparison

In order to compare different procedures for indirect DOC estimations, we selected six different methods from the literature. These were: 1) the method of Carter *et al.* (2012) that calculates DOC using absorbance at 270 nm and 350 nm, 2) the method of Wang & Hsieh (2001) that uses the area under the UV spectra between 250 nm and 350 nm to create a calibration for DOC, 3) a calibration curve created using absorbance at 254 nm, 4) a calibration curve created using absorbance at 400 nm, 5) a calibration created using the optimum absorbance wavelength derived from the DOC proxy assessment, and 6) the method of Peacock *et al.* (2013) that uses a calibration created using phenolic concentration. UV-vis and DOC analysis was conducted in the same manner as the DOC proxy assessment. Phenolic concentrations were determined using a method adapted from Box (1983). 0.25 ml of sample was added to a clear microplate well. 12.5 µl of Folin-Ciocalteau reagent was added followed by 37.5 µl of Na_2CO_3 (200 g L^{-1}). After 1.5 hours the absorbance was measured at 750 nm on a Molecular Devices M2e Spectramax plate-reader. Phenolic concentrations were then derived from the preparation of a standard curve using laboratory-prepared standards of known concentration (0, 1, 2, 4, 6, 8, 10, 15, 20 mg L^{-1}). All six methods were tested on two sets of samples from the Afon Ddu catchment; one set from ditch water, and one set from pore water. 48 water samples were used to create the ditch calibrations which were then used to model DOC for 47 samples. For the pore water set, 40

samples were used to create the calibrations and these were tested on 44 samples. Data analysis was performed using SPSS v16.0.1.

3.2.3. E ratio assessment

In order to assess how suitable E ratios are in characterising DOC from peatlands, we monitored surface and pore water in the Afon Ddu catchment, on an approximately monthly basis. Surface water was collected from four ditches on 25 occasions, from October 2010 to October 2012. Pore water was collected from four piezometers adjacent to each ditch on 23 occasions, from January 2011 to October 2012. UV-vis and DOC analysis was conducted in the same manner as the DOC proxy assessment. The investigated ratios were the E2:E3 ratio (250 nm : 365 nm), E2:E4 ratio (250 nm : 400 nm), E4:E6 ratio (465 nm : 665 nm), and SUVA (254 nm : DOC). To directly examine the molecular composition of DOC, size-exclusion chromatography (SEC) was performed on a limited number of samples. This was done using an Agilent PL-GPC 50 with a six point calibration of analytical grade standards: Poly(styrenesulfonic acid) sodium salt: 4300MM, 13000MM, 32000MM, 77000MM, 155000MM, Cyanocobalamin (vitamin B12): 1340MW.

3.2.4. Absorbance degradation experiment

In order to quantify the rate of absorbance degradation in stored samples we collected sixty five water samples from ditches in the Afon Ddu catchment on one day in August 2012. Samples were stored in the dark at 4^{o}C and analysed within one day. Samples were filtered through Whatman 0.45 μm cellulose nitrate filters and analysed using a Molecular Devices M2e Spectramax plate-reader, as for the DOC proxy assessment. After this, samples were reanalysed every week for 12 weeks.

3. Results

3.3.1. DOC proxy assessment

For all four sets of samples the best fit between DOC and absorbance occurred in the lower wavelengths, and declined as wavelength increased (fig.1). R2 was above 0.8 for some wavelengths in each of the four sample sets, indicating a strong correlation between DOC and absorbance. For pore water, OLF, and Alwen Reservoir samples the strongest fit between absorbance and DOC (indicated by the highest R2 and lowest residual variance) was found at 230 nm, but for ditch water the strongest fit was at 263 nm. Whilst the R2 of the piezometer and Alwen Reservoir samples began dropping immediately, the R2 for the other two sample

sets was relatively stable up to approximately 350 nm, and then decreased after that. For all samples sets the R2 values declined gradually, dropping below 0.7 in ditch water samples at wavelengths above 702 nm, and above 474 nm in pore water. In OLF and Alwen Reservoir samples the R2 dropped below 0.7 at 435 nm and 500 nm respectively. In the higher wavelengths the ditch, pore water and OLF samples show rapid, noisy fluctuations in R2 between adjacent wavelengths, but this is absent from Alwen Reservoir samples where R2 continues to smoothly decline to 800 nm. Additionally, pore water samples show a 'trough' between 670 nm and 710 nm where R2 rapidly decreases then increases, suggesting a weaker fit between DOC and absorbance at these wavelengths. Examination of the raw spectra shows that there is a small increase in absorbance between these wavelengths.

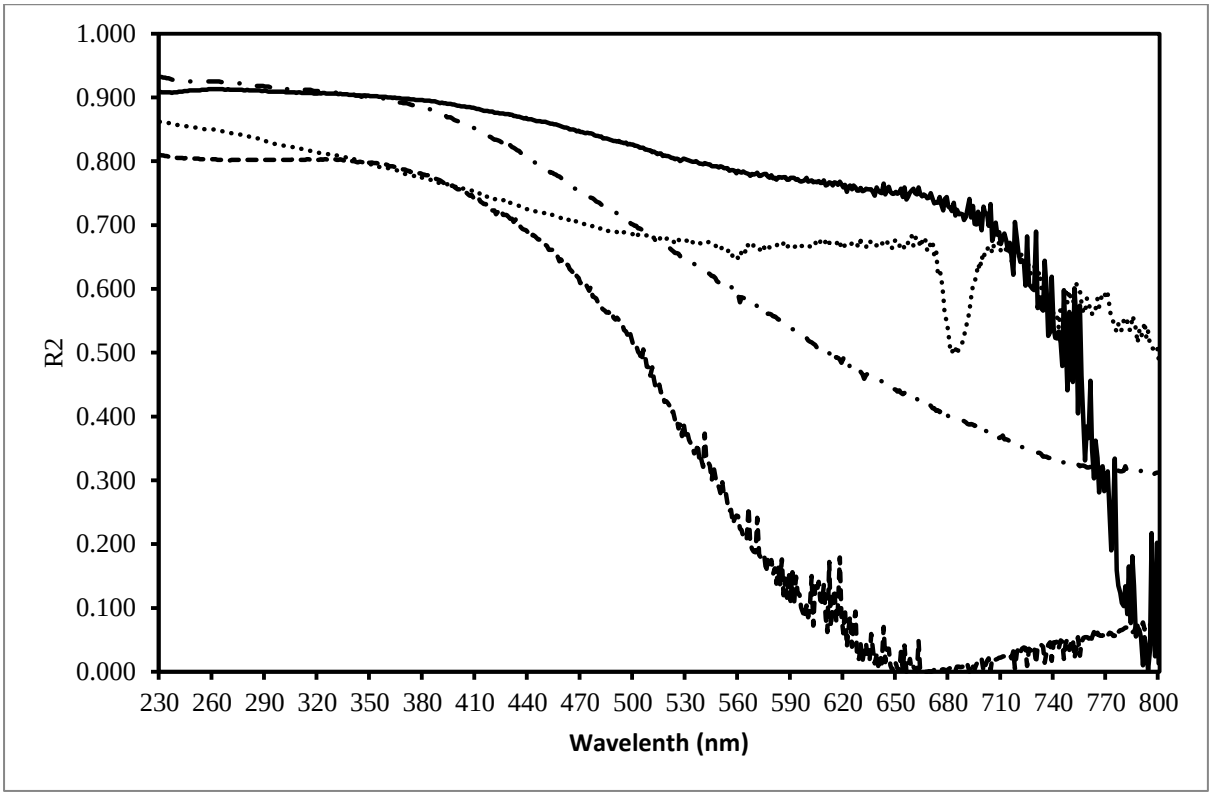

Figure 1. R2 values for regressions between DOC concentration and absorbance for wavelengths between 230 nm and 800 nm for four sites. Solid line = Afon Ddu ditch water *n*=108, dotted line = Afon Ddu pore water *n*=98, dashed line = Afon Ddu OLF water *n*=47, dashed and dotted line = Alwen Reservoir stream water *n*=40.

3.3.2. Procedural comparison

The six methods detailed in section 2.2 were used to calculate DOC. Using the results from the DOC proxy assessment, absorbance at 263 nm and 230 nm were chosen for ditch water and pore water samples, respectively. Table 3 shows the summary results. For ditch water the mean difference between modelled and measured DOC was lowest using an

absorbance proxy at 254 nm < abs 263 nm < method of Carter *et al.* (2012)/spectra area method < phenolics < abs 400nm. For pore water the mean difference between modelled and measured DOC was lowest using the method of Carter *et al.* (2012) < abs 254 nm/spectra area method < abs 230 nm < abs 400nm < phenolics. For both sample sets, the model R2 was considerably lower when using phenolic and 400 nm proxies. However, ANOVA revealed that there were no significant differences in either ditch water or pore water between measured DOC and modelled DOC calculated using any of the six methods. There was no significant difference between modelled DOC datasets for any of the six methods for ditch water or pore water.

The results of the DOC proxy assessment were partially reinforced; the wavelength with the highest R2 values from that analysis for pore water (230 nm) produced better calibration and model R2 values for this experiment when compared to 254 nm. For ditch water the wavelength that was selected on the basis of the DOC proxy assessment (263 nm) generated identical calibration and model R2 values as 254 nm.

Table 3. Summary results for six different methods of indirectly calculating DOC in ditch and pore water samples. 1) the method of Carter *et al.* (2012) that calculates DOC using absorbance at 270 nm and 350 nm, 2) the method of Wang & Hsieh (2001) that uses the area under the UV spectra between to create a calibration for DOC, 3) a calibration curve created using absorbance at 254 nm, 4) a calibration curve created using absorbance at 400 nm, 5) a calibration created using the optimum absorbance wavelengths (263 nm and 230 nm) derived from the DOC proxy assessment, and 6) the method of Peacock *et al.* (2013) that uses a calibration created using phenolic concentration. Mean diff is the mean difference between calculated and actual DOC, and SE is the standard error of the mean of this difference. Calibration R2 is the strength of the regression for each calibration of DOC and the method. The method of Carter *et al.* (2012) just uses absorbance to directly calculate DOC after model parameterisation and therefore has no calibration R2. Model R2 is the strength of the regression between measured and modelled DOC. n = 47 for ditch water and 44 for pore water.

Ditch water	Abs 270/350 nm	Spectra area	254 nm	400 nm	263 nm	Phenolics
Mean diff (mg L^{-1})	1.69	1.69	1.49	2.78	1.51	2.57
SE	0.24	0.15	0.14	0.21	0.14	0.37
Calibration R2	n/a	0.85	0.86	0.82	0.86	0.89
Model R2	0.97	0.98	0.98	0.93	0.98	0.91
Pore water	Abs 270/350 nm	Spectra area	254 nm	400 nm	230 nm	Phenolics
Mean diff (mg L^{-1})	3.20	3.61	3.61	5.41	3.75	7.49
SE	0.34	0.48	0.47	0.62	0.45	0.58
Calibration R2	n/a	0.68	0.72	0.55	0.75	0.47
Model R2	0.93	0.91	0.91	0.86	0.93	0.81

Despite the lack of a significant difference between calculated datasets, there were still systematic deviations for some of the models. For instance, a phenolics proxy consistently underestimated DOC concentrations for both pore water and ditch water, whilst an absorbance proxy at 400 nm consistently underestimated DOC for pore water. The pattern of over/underestimation was identical or similar for absorbance proxies in the UV range; all the samples that were overestimated using 254 nm in ditch water were also overestimated using 263 nm, and those overestimated using 254 nm in pore water were overestimated using 230 nm. These similarities did not exist between 254 nm and 400 nm however (table 4).

Table 4. Number of over- and underestimated DOC concentrations for the six different methods of indirectly calculating DOC in ditch and pore water samples. 1) the method of Carter *et al.* (2012) that calculates DOC using absorbance at 270 nm and 350 nm, 2) the method of Wang & Hsieh (2001) that uses the area under the UV spectra between to create a calibration for DOC, 3) a calibration curve created using absorbance at 254 nm, 4) a calibration curve created using absorbance at 400 nm, 5) a calibration created using the optimum absorbance wavelengths (263 nm and 230 nm) derived from the DOC proxy assessment, and 6) the method of Peacock *et al.* (2013) that uses a calibration created using phenolic concentration.

Ditch water	Abs 270/350 nm	Spectra area	254 nm	400 nm	263 nm	Phenolics
No. of overestimates	23	33	32	29	32	16
No. of underestimates	24	14	15	18	15	31
Pore water	Abs 270/350 nm	Spectra area	254 nm	400 nm	230 nm	Phenolics
No. of overestimates	13	17	23	8	25	9
No. of underestimates	31	27	21	36	19	35

By comparing the regression intercepts for the slope equations of the model calibrations, the minimum possible value of DOC that can be predicted by that method can be calculated. We refer to this as the lowest detection limit (LDL). Table 5 shows these values. For both sets of samples the spectra area method and a proxy at 254 nm performed comparatively well, but for ditch water a phenolics proxy was the most suitable, as evidenced by a negative intercept (i.e. the LDL was zero). For ditch water the largest value was 2.7 for a 400 nm proxy, but the pore water values were larger, with 8.23 at 400 nm being the largest such value.

Table 5. Regression slope intercepts (from the slope equation y = mx =b) for five different methods of indirectly calculating DOC in ditch and pore water samples. 1) the method of Wang & Hsieh (2001) that uses the area under the UV spectra between to create a calibration for DOC, 2) a calibration curve created using absorbance at 254 nm, 3) a calibration curve created using absorbance at 400 nm, 4) a calibration created using the optimum absorbance wavelengths (263 nm and 230 nm) derived from the DOC proxy assessment, and 5) the method of Peacock *et al.* (2013) that uses a calibration created using phenolic concentration. These values are the LDLs for calculated DOC.

Ditch water	Spectra area	254 nm	400 nm	263 nm	Phenolics
Intercept	2.23	2.14	2.70	2.17	-1.69
Pore water	Spectra area	254 nm	400 nm	230 nm	Phenolics
Intercept	-1.84	-4.89	8.23	-9.59	7.83

3.3.3. E ratio assessment

Overall means for all three E ratios were larger for pore water than ditch water, although this difference was only marginal for the E2:E3 and E2:E4 ratios. SUVA was higher for ditch water (table 6). Standard errors were small, except for the E4:E6 ratio where SEs were an order of magnitude larger. Figure 2 shows the monthly data. For both ditch and pore water the E4:E6 ratio showed considerable variation over time, whilst the E2:E3 ratio was the most stable. There was some evidence of shared trends in the E4:E6 ratio for both sample types, for example, the increase on the 5.7.11, and the peak on the 9.7.12.

Table 6. Means and standard errors for the four ratios examined. n = 100 for ditch water, n = 86 for pore water, except for pore water SUVA where n = 85.

	Ditch water		Pore water	
	Mean	SE	Mean	SE
E2:E3	3.65	0.02	3.70	0.01
E2:E4	6.42	0.07	6.77	0.05
E4:E6	5.99	0.38	7.37	0.44
SUVA	4.58	0.09	4.00	0.05

Based on the results from the SEC analysis there was no evidence of changes to the molecular weight of the DOC. Table 7 shows the various ratios for a set of four ditch water and three pore water samples, whilst figure 3 shows their respective chromatograms from the SEC. An examination of the SEC results reveals that there is no visible difference in molecular weight. There is little variation in each sample set for SUVA, E2:E3 and E3:E4, but the E4:E6 results cover a wide range of values, particularly for ditch water samples.

Table 7. Ratios for a set of four ditch water samples from January 2012, and three pore water samples from July 2012.

Ditch water	Ditch	E2:E3	E2:E4	E4:E6	SUVA
	1	3.85	6.95	5.66	3.34
	2	3.73	6.57	9.30	2.79
	3	3.93	7.36	12.38	4.07
	4	3.77	6.96	12.80	3.24
Pore water	Ditch	E2:E3	E2:E4	E4:E6	SUVA
	1	3.76	6.92	10.77	4.30
	2	3.73	7.00	12.14	4.10
	3	3.60	6.80	14.31	4.60

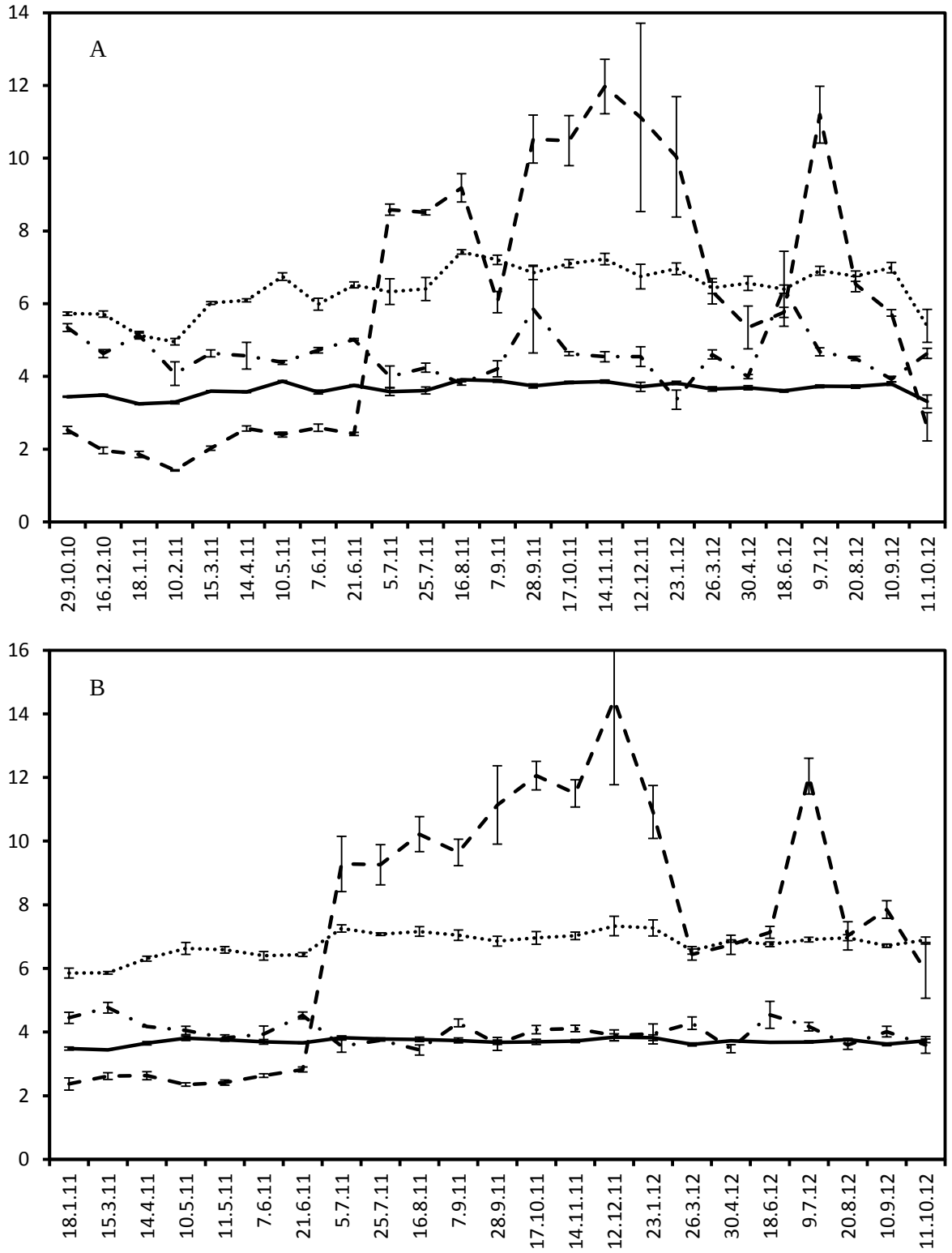

Figure 2. Monthly mean values for E2:E3 ratio (continuous line), E2:E4 ratio (dotted line), E4:E6 ratio (dashed line) and SUVA (dotted and dashed line) for A) ditch water and, B) pore water. For each month $n = 4$, with the following exceptions for pore water: $n = 3$ for 5.7.11, 25.7.11, 10.9.12, 11.10.12 and $n = 2$ for 15.3.11. For pore water SUVA only, $n = 3$ for 11.5.11.

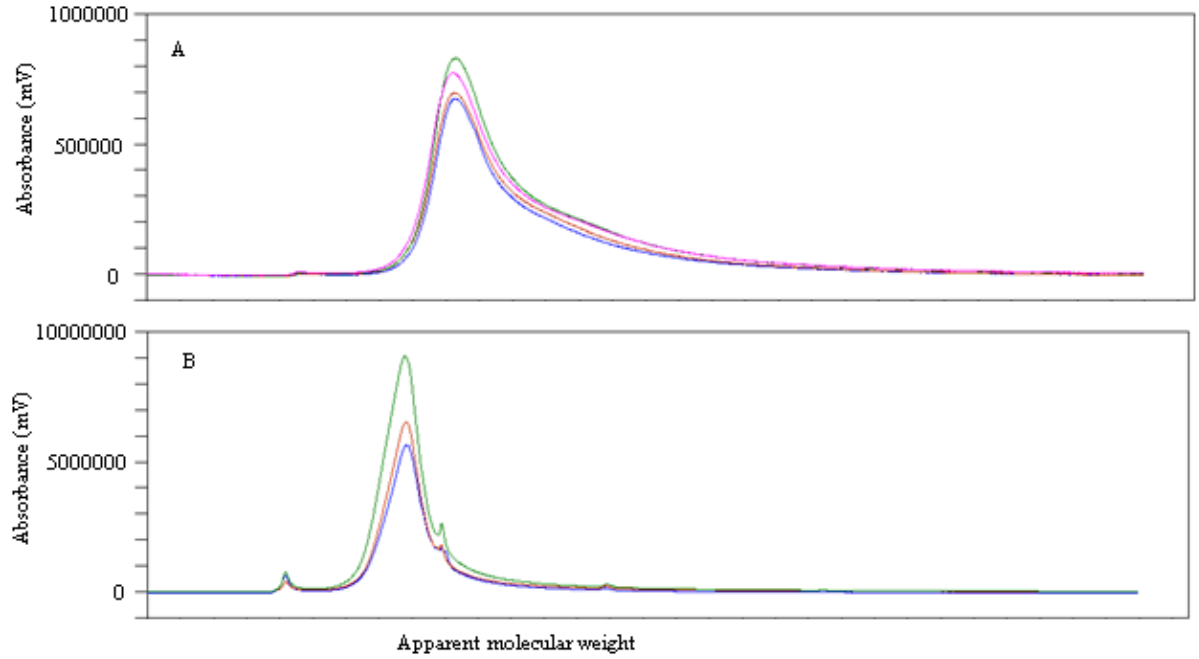

Figure 3. SEC chromatograms for A) four ditch water samples from January 2012 and B) three pore water samples from July 2012. Differences in chromatogram height are due to differences in DOC concentration. Note that the y axis scale is different on each graph.

3.3.4. Absorbance degradation experiment

After twelve weeks of repeated measurements there was no consistent decrease or increase in absorbance at any wavelength (fig. 4). Instead, the mean absorbance displayed small fluctuations. The mean difference in absorbance between the original and week 12 measurements were extremely small (table 8). ANOVA showed that there were no significant differences between the original absorbance values and any of the later weekly measurements for 250 nm, 365 nm, 400 nm and 465 nm. For 600 nm there was a significant difference between the original absorbance values and those measured during week 4. Although the fluctuations in mean absorbance are of a larger absolute magnitude at 250 nm, and decrease with increasing wavelength, when expressed as a percentage of the mean absorbance they are similar for all wavelengths, though slightly higher at 600 nm (table 8).

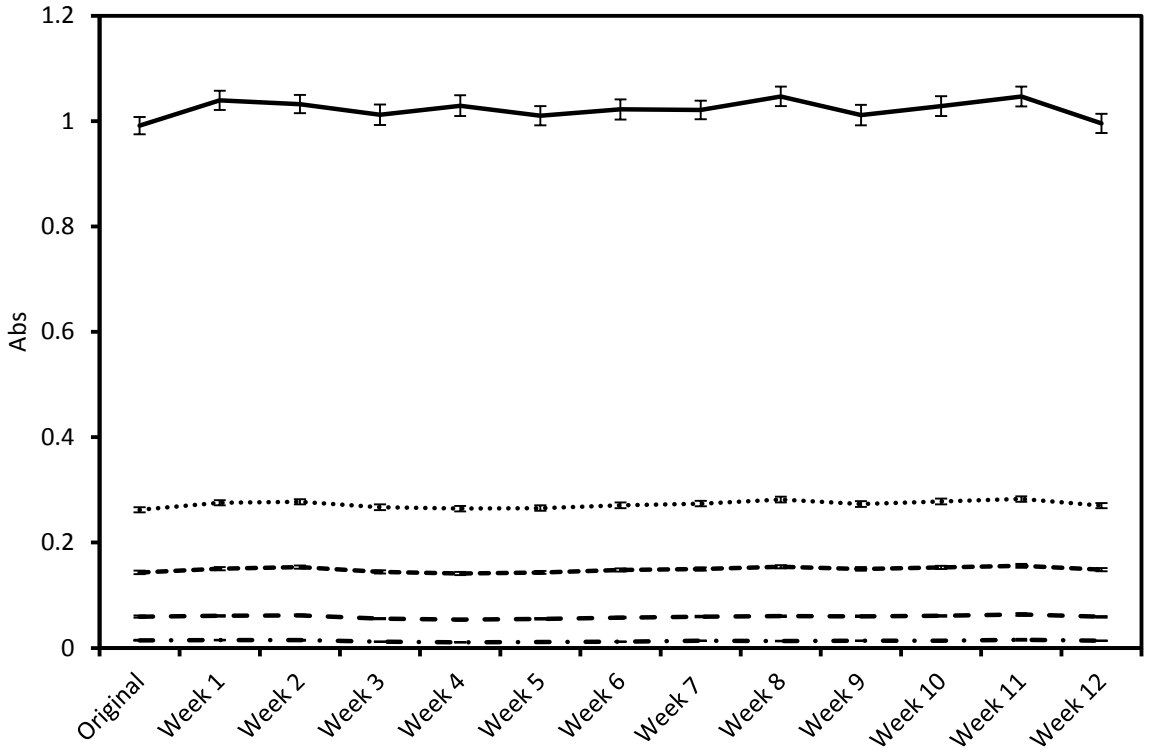

Figure 4. Mean absorbance values for five wavelengths, for a set of surface water samples (n = 65) that were analysed every week for twelve weeks. The wavelengths are 250 nm (solid line), 365 nm (dotted line), 400 nm (square-dotted line), 465 nm (dashed line) and 600 nm (dashed and dotted line). Error bars show standard error of the mean.

Table 8. The mean difference between the original absorbance measurements and week 12 absorbance measurements, and the mean percentage deviation of weekly measurements when compared to the original measurements.

Wavelength (nm)	254	354	400	465	600
Mean difference	0.004	0.008	0.005	0	-0.001
Mean % deviation	3.3	4.6	5.0	4.9	9.8

Examining the raw spectral data is another way to visually determine if there have been changes in the UV-vis properties of the water samples. Figure 5 shows a random selection of paired spectra for four samples. There is no obvious difference between the pairs for samples A and C, but samples B and D show more discrepancy, particularly in the low (<400 nm) wavelengths. However, the actual shape of the spectra were not visibly different.

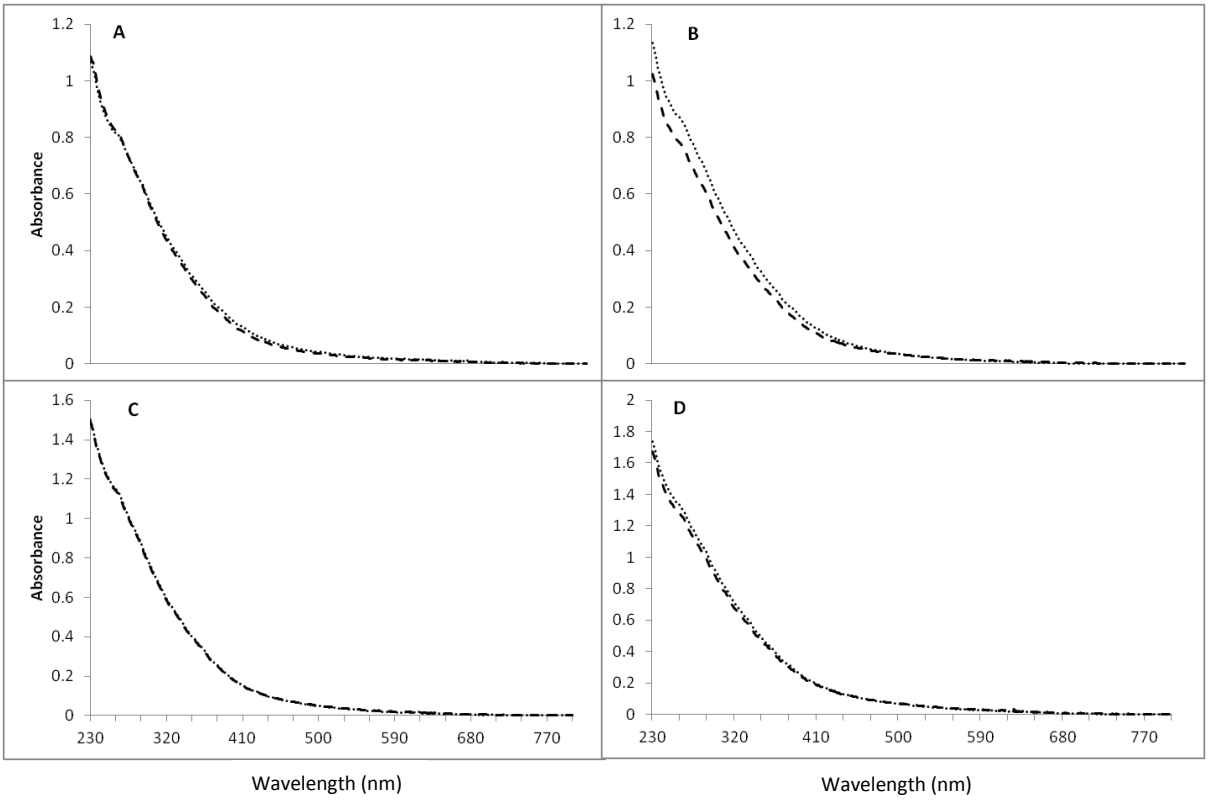

Figure 5. Paired UV-vis spectra for four water samples (labelled A, B, C, D). For each graph, the dashed line shows the spectra of the sample at the start of the 12 week analytical period, and the dotted line shows the spectra as measured during week 12.

3.4. Discussion

3.4.1. DOC proxy assessment

For all four data sets the fit between DOC and absorbance wavelength was strongest in the shorter wavelengths, and declined as wavelength increased. This is expected; for humic acids absorbance decreases as wavelength increases and therefore using a shorter wavelength would give higher resolution (Wang & Hsieh, 2001), a finding also reinforced by Peacock *et al.* (2013) who found that 254 nm was a more accurate proxy than 400 nm. For three of the sample sets the most robust proxy was 230 nm; the shortest wavelength investigated, whilst for ditch water samples 263 nm was found to be the best proxy. It is probable that this difference is derived from the exact aromatic moieties of the DOC, as numerous aromatic acids are present in natural waters (Thurman, 1985), and wavelengths such as 250 nm, 254 nm, and 280 nm have been associated with aromaticity (Peuravuori & Pihlaja, 1997, Weishaar *et al.*, 2003). For ditch water and OLF samples the fit between DOC and absorbance was relatively stable in the short wavelengths, suggesting that numerous wavelengths between 230 nm and 350 nm would function as equally accurate DOC proxies. This was not the case for pore water and Alwen Reservoir samples where R2 decreased immediately as wavelength increased from 230 nm. This indicates that ditch water and OLF

DOC contained a wide array of aromatic moieties which accordingly absorbed light in a wide range of the UV spectrum, whereas pore water and Alwen Reservoir samples had a much narrower aromatic fingerprint.

These findings call into question the use of longer wavelengths such as 400 nm as DOC proxies, and suggest that care should be taken when selecting a single wavelength as a DOC proxy. Although 230 nm gave the most accurate proxy for three out of the four sample sets here, it is inappropriate for certain waters, as NO_3^--N will interfere with absorbance at wavelengths shorter than 250 nm (Wang & Hsieh, 2001). The fact that different wavelengths were found to be accurate for pore water and surface water at the same site is not surprising, as Wallage & Holden (2010) demonstrated that the relationship between absorbance and DOC changed with factors such as peat layer, due to changes in the proportions of differently-coloured compounds that comprise DOC. Clay *et al.* (2012) noted similar changes after burning, where DOC concentration stayed the same but absorbance at 400 nm decreased as more years passed since the burn.

As far as we are aware, the style of the presentation of DOC proxy data (i.e. individual R2 values for regression between absorbance and DOC graphed against individual wavelengths) in figure 1 is completely novel. As such, it offers a new way of visualising absorbance data and provides new insights into the quality of dissolved organic matter. For example, the 'trough' in the pore water samples between 670 nm and 710 nm shows an absorbance region where the relationship between DOC and absorbance is weaker than that immediately above and below this region. This suggests that between these wavelengths there is a compound that absorbs light but is not DOC. As the samples in question are pore water it seems logical that this is caused by some compound leaching into the water. It has been proposed that the boundary between oxic and anoxic peat layers is important in the formation of humic-iron colloids (Heikkinen, 1994), and iron is known to contribute to water colour at 420 nm (Kritzberg & Ekstöm, 2012) as well as interfering with UV absorbance analysis (Doane & Horwáth, 2010). The unknown compound interferes at much longer wavelengths however, and therefore is likely to be something different. Iron is present in the waters of the Afon Ddu catchment (Austnes *et al.*, 1010) and so the contaminant could be a colloidal 'green rust' (Satapanajaru *et al.*, 2003) such as Fe(II) Fe(III) hydroxyl carbonate which has an absorbance peak at 650 nm (Hansen, 1989). Green rusts have been found in hydromorphic soils (Génin *et al.*, 1998). Iron hydroxide is another possibility, as it is common in natural waters (Hem & Cropper, 1959) and absorbs light at 750 nm (Box, 1983).

Other similar iron compounds may exist that could interfere with absorbance as these wavelengths.

3.4.2. Procedural comparison

There was no significant difference between measured and modelled DOC for any of the six methods used to calculate DOC. It might be that significant differences would be found if the different methods were tested on larger sample sizes, as long-term environmental monitoring of waters typically generates large amounts of data. The best method was found to be an absorbance proxy at 254 nm for surface water, and the method of Carter *et al.* (2012) that calculates DOC using absorbance at 270 nm and 350 nm for pore water. The model that performed the least accurately was an absorbance proxy at 400 nm for surface water, and a phenolics proxy for pore water. This was due to 400 nm consistently underestimating DOC, and phenolics consistently overestimating DOC in samples of these types.

These results are at odds with those of Wang & Hsieh (2001) who found that using the area under the spectra was a more accurate proxy than a single wavelength. The R2 of the model calibrations was slightly higher for a proxy at 254 nm compared to one using the area under the spectra between 250 nm and 350 nm. One possible explanation for this is that the increased number of measurements allows more scope for error to be introduced into the calculations. For example, using absorbance at 254 nm from 20 water samples to produce a DOC calibration needs 20 absorbance measurements. To produce the same calibration using the spectra area method, 2000 absorbance measurements are needed (absorbance at every wavelength between 250 nm and 350 nm); two orders of magnitude higher. This large number of measurements may therefore lead to more incidences of analytical error which, however slight, accrue over time and lead to a less accurate DOC model. Likewise, the results are partially at odds to those of Carter *et al.*, (2012) who found that using a two wavelength model increased R2 by 0.02 or 0.05 when compared to a UV proxy at 270 nm or 350 nm. We report an increase in R2 of 0.02 for pore water when using a two wavelength model rather than absorbance at 254 nm. However, for surface water a single wavelength model using 254 nm was better than the two wavelength model by 0.01.

The results of the DOC proxy assessment were echoed for this analysis; 230 nm, the wavelength that was selected from that experiment for pore water, improved the R2 values of the model and calibration when compared to a 254 nm proxy. However, the calibration and model strengths for surface water were the same for wavelength selected from the DOC proxy assessment (263 nm) and 254 nm.

Wallage & Holden (2010) found that using a proxy at 400 nm gave low detection limits of DOC, as calculated by taking the regression intercept of the model calibration. For surface water all models performed well, with 2.7 mg L^{-1} being the highest LDL. For pore water the LDLs showed more variation, with 8.23 mg L^{-1} being the highest LDL. This is similar to results from Wallage & Holden (2010) who found that LDLs using 400 nm ranged from -0.77 mg L^{-1} to 10.32 mg L^{-1} for pore water in English blanket bog. High LDLs indicate that a large amount of DOC is undetectable using that method. For instance, a high LDL at 400 nm suggests that much of the DOC is uncoloured, and therefore does not absorb light at this wavelength. This is reinforced by the much lower LDL for 254 nm, as the aromatic compounds that dominate humic substance absorb light in this region (Edzwald *et al.*,1985). Our results also show some negative LDLs. These calibrations theoretically allow DOC to be calculated down to 0 mg L^{-1}.

The data here support the conclusion of the DOC proxy assessment and of Peacock *et al*. (2013), in showing that 400 nm should be avoided as a DOC proxy if possible. Absorbance at approximately 400 nm can be subject to interference by iron concentrations (Kritzberg & Ekstöm, 2012). Additionally, the relationship between DOC and absorbance at 400 nm has been demonstrated to show considerable variation within the same catchment, according to changes in vegetation (Gough *et al.,* 2012). As such, using 254 nm as a proxy gave a higher R2 value for both the calibration and testing of a DOC : absorbance model, and allowed DOC to be modelled at lower concentrations. Wallage & Holden (2010) state that "*problems that we have identified in this paper will have to be overcome including problems of low DOC detection limits when using absorbance proxies.*" The results presented here suggest that this statement is true of 400 nm, but not necessarily for 254 nm. Additionally, our results contradict the idea presented by Grayson & Holden (2012) that wavelengths under 300 nm are not suitable as DOC proxies. Their argument is based on the assertion that wavelengths under 300 nm show large and rapid fluctuations when measured continuously in streamwater using a spectrophotometer, compared to longer wavelengths that show cleaner signals. However, it is highly likely that the rapid fluctuations in absorbance below 300 nm are real, not artefacts, and are changing as DOC concentrations also fluctuate according to environmental conditions such as precipitation events. Other data gathered using the same type of instrument has shown that DOC concentrations can indeed fluctuate rapidly (Koehler *et al.,* 2009), and the use of continuous monitoring technology has revealed that water chemistry determinands are actually highly dynamic, and fluctuate on an hourly basis (Kirchner *et al.,* 2004). Longer wavelengths such as 400 nm and 600 nm will not show these

fluctuations to the same precision as a large proportion of DOC is uncoloured (Thurman, 1985) and therefore not detectable outside of the UV spectrum.

The two wavelength method of Carter *et al.,* (2012) is clearly a useful DOC proxy. Using the model parameters described in their paper gave accurate predictions of DOC (data not shown here) but small changes in the parameters improved the calculations for the site investigated. The parameters cited by Carter *et al.,* (2012) were generated using a large number of samples which were all taken from surface water, and as such were unsuitable for calculating DOC in pore water. However, calibrating the model parameters using DOC and absorbance data then produced an excellent fit for pore water. This suggests that the model can potentially have widespread applicability for different types of water sample, provided a calibration dataset is available.

3.4.3. E ratio assessment

Over approximately two years, the E2:E3 ratio, E2:E4 ratio, and SUVA were relatively stable and displayed small fluctuations within a narrow range of values for both ditch water and pore water. In contrast, the E4:E6 ratio was subject to large, rapid changes, although values were consistent with those from the literature (Thurman, 1985). To some extent the fluctuations in all four ratios will be driven by seasonal changes (Jaffé *et al.,* 2008). For example, storm events will contribute increased volumes of low DOC surface run-off into ditches, and therefore dilute ditch water DOC (Clark *et al.,* 2007). Field observations supported this hypothesis, with water in ditches being visibly more coloured during dry periods, and appearing clearer after heavy precipitation events.

The E4:E6 ratio is often used as a measure of humification, and changes to it following peatland rewetting have been cited as an indicator of biogeochemical changes (Wallage *et al.,* 2006, Wilson *et al.,* 2011). The use of the E4:E6 ratio is questionable however, judging by the way it fluctuated at the study site where no anthropogenic changes were inflicted upon the monitored ditches. In agreement with our results Park *et al.* (1999) noted consistent E2:E4 ratios but varying E4:E6 ratios when comparing samples, and O'Driscoll *et al.* (2006) found no relationship between the E4:E6 ratio and DOC composition. They suggested that the E4:E6 ratio is not suitable for freshwater DOC analysis, as did Peuravuori & Pihlaja (1997).

The lack of difference in molecular weight between samples, as evidenced by SEC, and the associated lack of difference in the E2:E3 and E2:E4 ratios suggest that future peatland work should use these measurements to indirectly assess the composition of DOC.

However, the aforementioned ability of iron to interfere with measurements around 400 nm (Kritzberg & Ekstöm, 2012) means that the accuracy of the E2:E4 ratio (and E4:E6 ratio) can be compromised in waters with high iron concentrations.

3.4.4. Absorbance degradation experiment

There was no consistent decrease or increase in absorbance for any wavelength after 12 weeks of repeated UV-vis analysis, and absorbance values after 12 weeks were remarkably similar to those measured at the start of the experiment. This is unexpected; although not always explicitly stated, there is an implied understanding that absorbance must be measured as soon as possible after water samples have been collected. Carter *et al.*, (2012) noted a decrease of 5% after 50-120 days, and this value falls within the observed range of fluctuations found here. It is therefore plausible that the 5% value from Carter *et al.*, (2012) is not the result of a steady decrease in absorbance due to degradation, but is just a random fluctuation similar to those reported here. Although their 5% figure is only mentioned in passing, it appears that this percentage was reached due to one-off re-analysis of older samples, rather than a comprehensive temporally-repeated experiment. Comparisons of UV-vis spectra from samples at the start of the experiment and after 12 weeks were very similar, with only slight differences in absorbance, and with no deviations in the shape of the spectra. The probable origin of the non-significant fluctuations in absorbance over the course of the experiment is human and machine error; for example, small discrepancies when pipetting samples for analysis.

It is important to state that there are caveats to this result. For example, calcium can cause DOC to come out of solution and to flocculate (Römkens & Dolfing, 1998), and this can therefore be problematic where water samples are taken from rich fens. In such circumstances, absorbance must be measured before samples begin to flocculate.

An important inference of the lack of observed decrease in absorbance over time is that there must also be no change in DOC concentration. There is a substantial body of literature concerning sample preservation for marine environments, though some of it is contradictory. For instance, Sugimura & Suzuki (1988) recommended filtration and cold storage, as they concluded that both freezing and acidification did not give reliable results. Contrary to this, Tupas *et al.* (1994) suggested that cold storage (with or without filtration) resulted in a loss of DOC, and that freezing or acidification were preferable. There is less literature concerning non-marine systems but the US Environmental Protection Agency recommends that water utilities should preserve samples through filtration and acidification

(Karanfil *et al.,* 2002). The absence of an observed decrease in DOC concentration here suggests that filtration at 0.45 µm and cold storage in the dark was sufficient to preserve samples from bacterial or chemical degradation. This is obviously not true for all water types and samples, but more research is clearly needed to determine if it is universally true for peatland systems.

3.4.4. Conclusions

The results presented here go some way towards clarifying and challenging the paradigms of UV-vis spectroscopy for the study of natural waters. Out of the various DOC proxies that were investigated, 400 nm was found to consistently perform with less accuracy when compared to 254 nm, and therefore should be avoided as a DOC proxy. Other wavelengths such as 230 nm and 263 nm also acted as robust proxies, depending on the site and sample type they were tested on. The two-wavelength method of Carter *et al.* (2012) was found to estimate DOC remarkably well for surface waters, and parameterisation further improved the model, although a single wavelength proxy at 254 nm still performed marginally more accurately. For pore water the two wavelength method was the most accurate after parameterisation. Further investigations of the two wavelength method may be worthwhile, as the most accurate proxy may differ between sites. If funds and equipment are available a calibration can be established to give the greatest accuracy possible. If direct DOC analysis for a calibration is not possible, then the 'universal calibration' parameters provided by Carter *et al.,* (2012) should still provide robust DOC estimations for surface water. This therefore enables DOC monitoring to proceed in situations where it would otherwise be too expensive; for instance, low-budget peatland restoration projects.

In summary, the most robust proxy for DOC depends on a variety of factors, such as the strength of the calibration regression, the intercept of the calibration regression which determines the LDL, and whether a proxy systematically overestimates or underestimates DOC concentration. To characterise DOC, we suggest the use of the E2:E3 ratio, E2:E4 ratio, and SUVA, and recommend avoiding the use of the E4:E6 ratio due to the large temporal variations it can be susceptible to. It is easy to criticize those projects where DOC is not measured directly, but a lack of available funds can be restrictive, and any attempt to quantify DOC dynamics, particularly in relation to land-use changes such as peatland ditch blocking, should be lauded. We suggest here that the use of indirect DOC measurement does not necessarily invalidate the data produced from such projects.

Finally, the results from the 12 week degradation experiment suggest that absorbance, and therefore DOC concentrations, do not necessarily decline during storage. This will not be the case for all systems, but for the peatland catchment investigated here it was found that filtration at 0.45 μm followed by storage in the dark at 4^{o}C was sufficient to preserve surface water samples.

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The effect of peatland drainage and rewetting on extracellular enzyme activities

4.1. Introduction

Northern peatlands store an estimated 547 Gt of carbon (Yu *et al.*, 2010), making them important natural sinks when considering global carbon cycling. However, extensive degradation has occurred as peatlands are drained for forestry and agriculture, and peat harvested for various uses. For UK blanket bog, drainage is usually achieved through the digging of drainage ditches, which might typically be 0.5 m deep with 15 m spacing between ditches (Stewart & Lance, 1991). In the UK this was mainly done in the 1960s and 1970s for agriculture. The effect of ditches is to lower the water table, and this is directly dependent on the hydraulic conductivity of the peat. As blanket bogs have low hydraulic conductivity (Galvin, 1976) they are resistant to drainage. Nevertheless, long-term drainage at a relatively high density (with drain spacing in the order of 10 m) does lead to the establishment of deeper water tables (Holden *et al.*, 2011), although this results in no real improvement in grazing value for livestock (Wilson *et al.*, 2011a).

Water table drawdown and drainage alters the peatland carbon balance, leading to increased carbon dioxide (CO_2) fluxes but decreased methane (CH_4) fluxes (Freeman *et al.*, 1993, Martikainen *et al.*, 1995) from the soil to the atmosphere. In some cases this can convert the peatland sink into a net source of carbon (Salm *et al.*, 2009). It also results in enhanced concentrations of dissolved organic carbon (DOC) (Wallage *et al.*, 2006) which, when chlorinated during water treatment, can form harmful by-products (Fenner *et al.*, 2001, Chow *et al.*, 2003). To reverse these detrimental effects, numerous peatland restoration projects have been initiated in the UK. Sites that have solely been ditched (i.e. with no peat harvesting) are restored by blocking the drainage ditches (i.e. rewetting), typically by constructing dams made of such materials as peat, heather bales, or plastic (Armstrong *et al.*, 2010). The aim of such projects is to return the water-table to pre-drainage levels. Some success has been observed on blanket bog; 6-7 years after rewetting, Holden *et al.* (2011) observed that a ditch-blocked site had hydrological functioning intermediate between a pristine site and drained site. Similarly, Wilson *et al.* (2011b) recorded an average water table increase of 2 cm (from approximately -10 cm to -8 cm) after ditch-blocking, and Worrall *et al.* (2007) noted a 9 cm mean increase (the study does not cite the magnitude of the drainage drawdown previous to this).

One biogeochemical aspect of drainage and rewetting that has received little attention is the effect on soil decomposition mediated by extracellular enzyme activity. These enzymes are involved in both gaseous and fluvial peatland carbon cycling (Freeman *et al.*, 1997) and under the anaerobic conditions that exist in peat soils their activity is restrained. Recalcitrant phenolic compounds are released by plants (Wetzel, 1992) and degraded by the enzyme phenol oxidase, which has limited activity in peatlands due to the acidic pH and low oxygen content (Pind *et al.*, 1994, Tahvanainen & Haraguchi, 2013). The build up of phenolics in turn inhibits the activity of hydrolase enzymes (Wetzel, 1992), resulting in low rates of decomposition. Conversely, increased peat aeration is thought to stimulate phenol oxidase activity, lowering phenolic concentrations, and thus removing the inhibitory effect on hydrolase enzymes (Freeman *et al.*, 2001a). As well as oxygen, increased temperatures increase phenol oxidase activity (Jassey *et al.*, 2011). This stimulation of phenol oxidase is not due to reestablishment of enzyme activity, but has been experimentally demonstrated to result from increased synthesis of phenol oxidase by the microbial community (Fenner & Freeman, 2011). It can therefore be hypothesised that long-term peatland drainage would lead to increased phenol oxidase activity, reduced phenolic concentrations and increased hydrolase activity, thereby resulting in greater overall soil decomposition rates and contributing to carbon loss (*hypothesis 1*). Theoretically, ditch blocking would reverse this by raising the water table, and leading to suppressed phenol oxidase activity, increased phenolic concentrations and reduced hydrolase enzyme activity (*hypothesis 2*). The aim of this study was to test these two hypotheses using three sites located within a large a Welsh peatland. As a caveat, it is important to acknowledge that this is a small scale study, and that changes to biogeochemical cycling at this scale will not necessarily translate into widespread catchment scale changes.

4.2. Materials and Methods

4.2.1. Study sites and treatments

The study was carried out on the Migneint blanket bog, in Snowdonia National Park, north Wales (UK). It includes areas of M18 (*Erica tetralix-Sphagnum papillosum*), M19 (*Calluna vulgaris-Eriophorum vaginatum*), and M20 (*Eriophorum vaginatum*) according to the JNCC National Vegetation Classification (NVC) (Elkington *et al*, 2002). Three sites on the Migneint were used which were within approximately 3km of one another. Table 1 gives further details of the sites.

Table 1. Site and treatment details

Site	Bryn Du	Llyn Serw	Ffynnon Eidda
Lat	52.99 N	52.97 N	52.97 N
Lon	3.82 W	3.82 W	3.84 W
Height ASL (m)	450	460	490
Treatment	Control (undrained)	Heather bales vs open ditches	Peat dams vs reprofiled ditches vs open ditches
Date of blocking	N/A	Aug-Sept 2008	Feb-11
Dominant vegetation	*Calluna*, with flushes of *Juncus*	*Calluna*	*Calluna*

Three different methods of ditch blocking were examined. The Llyn Serw site was blocked in August-September 2008. The experimental part of the site comprises a transect across one ditch that has been blocked by infilling with heather bales and a second transect across an open control ditch. The two ditches are separated by an infilled 'buffer' ditch. The Ffynnon Eidda site was blocked in February 2011. The replicated experiment at this site comprises four ditches that have been left open as controls, and eight that have been blocked using two different methods. Four have been blocked using peat dams. The peat is extracted from 'borrow pits' adjacent to the ditch. The other four have been blocked using a reprofiling technique. This involves the ditch vegetation being removed, and the peat bottom being compressed to destroy any natural pipes that may be present. The ditch is then infilled with peat and the vegetation is replaced. As in the previous treatment peat dams are also constructed along the ditch. This experimental design is relatively novel, as many ditch experiments have open and blocked ditches on different sites, lack comparable controls, or lack pre- and post-restoration data. At Llyn Serw and Ffynnon Eidda, blocked and open ditches are both included in the same site. The Bryn Du site contains four control plots on intact blanket bog that have not been ditched.

All three sites are operated as part of three distinct projects, but a comparison of their data is useful. Data from Llyn Serw can be used to show the impact of ditch blocking two years after rewetting, whilst data from Ffynnon Eidda demonstrates the immediate effect. Bryn Du can be used as a control reference point to show the impact of long term drainage at the control ditches of both Llyn Serw and Ffynnon Eidda.

4.2.2. Sampling

Sampling took place at Llyn Serw every three months throughout 2010: in March, June, September and December. At both the open and blocked ditch transects of four sampling points were established running across the ditch. Each ditch had one sampling point adjacent to the ditch on either side, then another approximately 1 m further away, again on either side. At Ffynnon Eidda one sample was taken from each ditch, and sampling took place during 2011: in June, July, August, September, and November. At Bryn Du four samples were taken (one from each control plot). Sampling took place approximately every month between November 2007 and December 2011.

Soil samples were taken from 10 cm depth. Each sample actually comprised 2-4 sub-samples of soil to minimise the influence of spatial variance in enzyme activity. Samples were stored in the dark at field temperature before analysis. Soil water content was determined by weighing a portion of sample, drying overnight in an oven at 105 ^{o}C, and then re-weighing.

Water samples were taken directly from the ditches at Ffynnon Eidda. Water samples at Llyn Serw were extracted via piezometers at a depth of 20 cm, along the same 4-point transect described above for soil sampling. Samples at Bryn Du were extracted using Rhizon samplers (Rhizosphere Research Products) at a depth of 10cm. Samples were stored in the dark at field temperature.

4.2.3. Phenol oxidase analysis

Phenol oxidase activity was measured using a method modified from Pind *et al.* (1994). A small amount of soil (approximately 1 cm^3) was weighed and combined with 9 ml of ultra-pure water in a stomacher bag. This was homogenized for 30 seconds using a Seward Stomacher 80. Six replicates of 750 µl of homogenate were extracted into centrifuge vials; of these, 750 µl of ultra-pure water was added to three replicates (as blanks), and 750 µl of 10 mM L-DOPA (L-3,4-dihydroxyphenylalanine) (Sigma-Aldrich) was added to the other three. Samples were then left at field temperature for 9 minutes, before being centrifuged at 10,000 rpm for 5 minutes to terminate the reaction. 300 µl of supernatant was then transferred to a microplate and absorbance measured at 460 nm using a Molecular Devices M2e Spectramax plate-reader. The mean absorbance of the three blank replicates was subtracted from the mean absorbance of the three L-DOPA replicates, and phenol oxidase activity calculated according to the Beer-Lambert Law and the molar absorption coefficient

for phenol oxidase (37000). As in Toberman *et al.* (2008a) no pH buffer was used so as to simulate field conditions as accurately as possible.

4.2.4. Hydrolase analysis

Analysis of hydrolase activity was measured using a method modified from Freeman *et al.* (1995). Soil samples were homogenized as for the phenol oxidase analysis, although 7ml of methylumbelliferone- (MUF)substrates was used in place of ultra-pure water. Four hydrolase enzymes were analysed using the following substrates: MUF-β-D-glucoside (β-glucosidase), MUF-sulphate (sulphatase), MUF-N-acetyl-D-glucosamine (chitinase), and MUF-β-D-xylopyranoside (xylosidase), all at 400 μM concentration. After homogenization, stomacher bags were incubated at field temperature for 60 minutes, and1.5 ml of homogenate was transferred to a centrifuge vial before centrifuging for 5 minutes at 10,000 rpm. 300 μl of supernatant was extracted onto a microplate. Standard curves were prepared using 0-40 μM MUF-free acid and soil samples, to correct for the quenching effect of phenolics. Fluorescence was measured at 450 nm emission and 330 nm excitation with a slit setting of 2.5 nm, using a Molecular Devices M2e Spectramax plate-reader.

4.2.5. Phenolics analysis

Phenolic concentrations were determined using a method adapted from Box (1983). 0.25 ml of sample was added to a clear microplate well. 12.5 μl of Folin-Ciocalteau was added, followed by 37.5 μl of Na_2CO_3 (200g L^{-1}) to buffer the reaction. After 1.5 hours the absorbance was measured at 750nm on a Molecular Devices M2e Spectramax plate-reader. Phenolic concentrations were then derived from the preparation of a standard curve using laboratory-prepared standards of known concentration.

4.2.6. Additional water analysis

Sulphate concentrations were determined using either a Dionex DX-120 Ion Chromatograph with AS40 Autosampler, or a Metrohm 850 Professional IC with 858 Professional Sample Processor. DOC concentrations were analysed using an Analytical Sciences Thermalox Total Carbon analyser after filtering samples through Whatman 0.45 μm cellulose nitrate filters. Samples were acidified (pH < 3) and sparged with nitrogen to remove any inorganic carbon. Specific absorbance at 254 nm (SUVA) was used to investigate the molecular composition of DOC. Water samples were filtered through Whatman 0.45 μm cellulose nitrate filters and absorbance was measured using a Molecular

Devices M2e Spectramax plate-reader. Results were corrected against blanks of ultrapure water. Samples were analysed for DOC using an Analytical Sciences Ltd Thermalox Total Carbon analyser.

4.2.7. Statistical analysis

Statistical analysis was carried out using SPSS v16.0.1 (IBM Corporation, http://www-01.ibm.com/software/analytics/spss/products/statistics/). After testing for normal distribution and equal variance, ANOVAs and repeated-measures ANOVAs with Tukey HSD post-hoc tests were carried out to test differences between treatments at Ffynnon Eidda for each month. Where data did not meet these assumptions the non-parametric Kruskal-Wallis test was used. For comparisons of two treatments, t-tests were used, or the non-parametric Mann-Whitney test.

4.3. Results

4.3.1. Effect of ditch blocking on enzyme activity and phenolics

At Ffynnon Eidda, 4-9 months after ditch-blocking, there was no significant difference between treatments for the activity of β-glucosidase, xylosidase or chitinase. There was a significant difference for sulphatase; activity was higher in the control ditches compared to the reprofiled ditches (fig.1). Figure 2 displays the data as total hydrolase activity. There was no significant treatment effect on phenol oxidase activity (fig.3).

At Llyn Serw, 18-27 months after ditch-blocking, a repeated-measures ANOVA found no significant differences in hydrolase or phenol oxidase activity. Activities of both phenol oxidase and hydrolases were lower at Llyn Serw when compared to Ffynnon Eidda. Total mean hydrolases ranged between 20.4 – 90.6 n moles g^{-1} min^{-1} MUF released at Ffynnon Eidda, and between 5.5 – 13.6 n moles g^{-1} min^{-1} MUF released at Llyn Serw. Phenol oxidase activity ranged between 6.0 – 29.2 nmol dicq g^{-1} min^{-1} at Ffynnon Eidda, and between 6.8 – 19.9 nmol dicq g^{-1} min^{-1} at Llyn Serw. Mean phenolic concentrations ranged from 4.2 – 8.7 mg L^{-1} at Ffynnon Eidda and 4.0 – 8.6 mg L^{-1} at Llyn Serw, with no significant treatment difference at either site (figures 6 and 7).

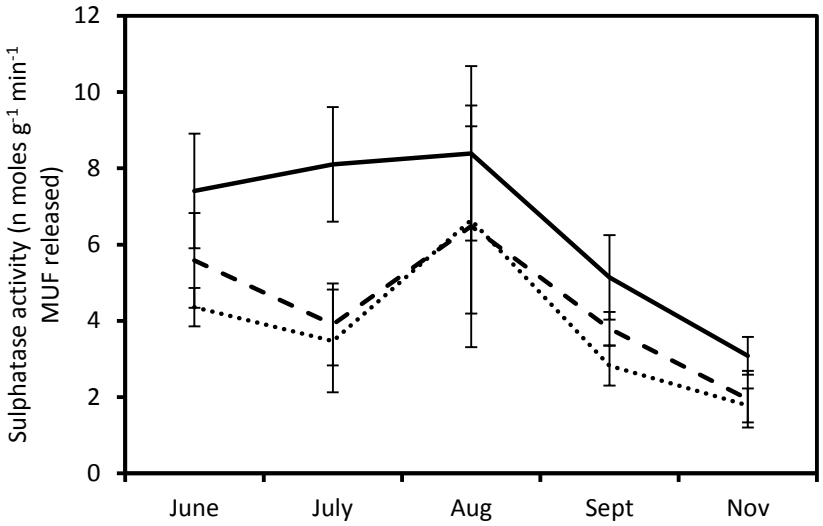

Figure 1. Mean sulphatase activity (n moles g^{-1} min^{-1} MUF released) for open control ditches (continuous line), reprofiled ditches (dotted line) and dammed ditches (dashed line) at Ffynnon Eidda during 2011. n=4 samples for each treatment. Errors bars show standard error of the mean. Repeated-measures ANOVA shows a significant difference ($p<0.05$) between control and reprofiled ditches.

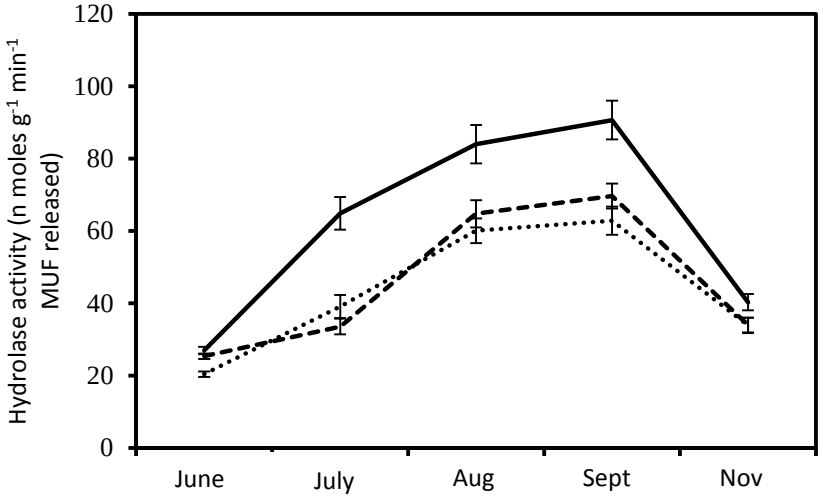

Figure 2. Total mean hydrolase activity (n moles g^{-1} min^{-1} MUF released) (i.e. sum of mean β-glucosidase, sulphatase, xylosidase and chitinase activity) for open control ditches (continuous line), reprofiled ditches (dotted line) and dammed ditches (dashed line) at Ffynnon Eidda during 2011. n=4 samples for each treatment. Errors bars show standard error of the mean. The only enzyme to show significant difference was sulphatase (refer to fig. 1).

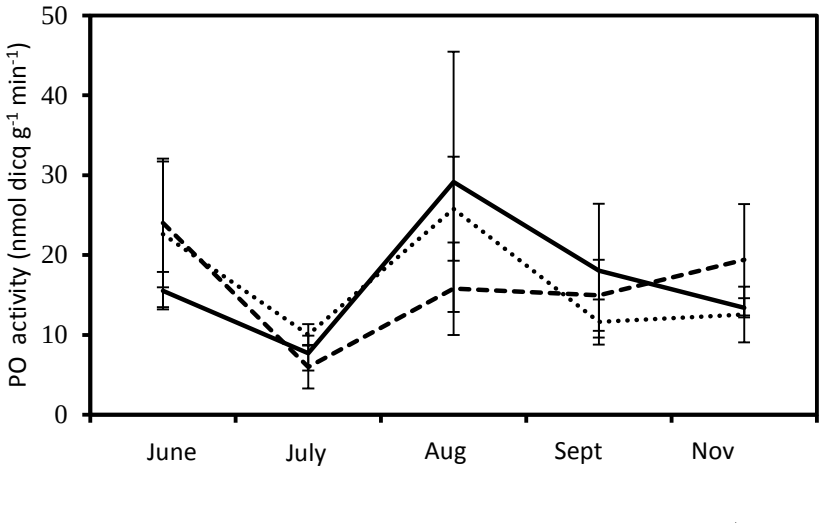

Figure 3. Mean phenol oxidase activity (nmol dicq g^{-1} min^{-1}) for open control ditches (continuous line), reprofiled ditches (dotted line) and dammed ditches (dashed line) at Ffynnon Eidda during 2011. n=4 samples for each treatment. Errors bars show standard error of the mean. There is no significant difference in activity.

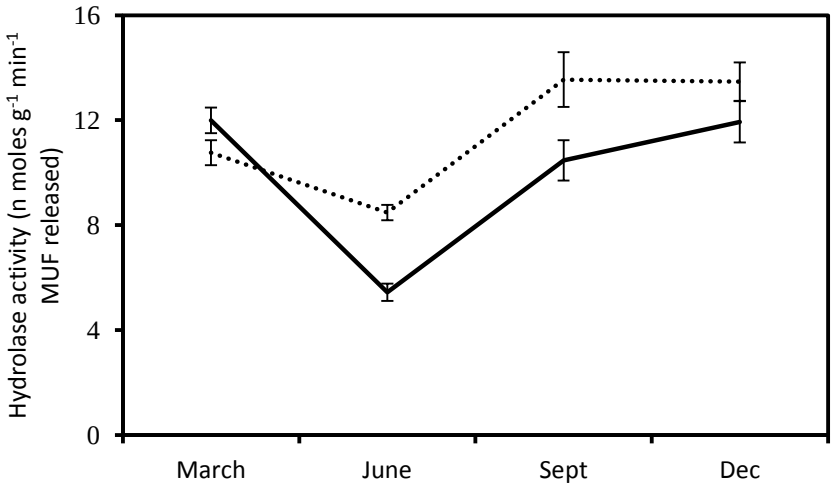

Figure 4. Total mean hydrolase activity (n moles g^{-1} min^{-1} MUF released) (i.e. sum of mean β-glucosidase, sulphatase, xylosidase and chitinase activity) for open control (continuous line) and blocked ditches (dashed line) at Llyn Serw during 2010. n=4 samples for each treatment. Errors bars show standard error of the mean. There is no significant difference in activity.

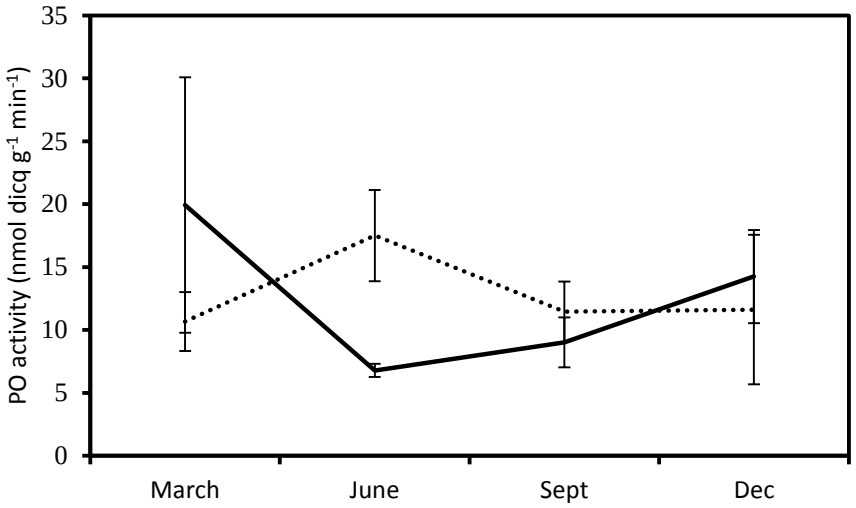

Figure 5. Mean phenol oxidase activity (nmol dicq g^{-1} min^{-1}) for open control (continuous line) and blocked ditches (dashed line) at Llyn Serw during 2010. n=4 samples for each treatment. Errors bars show standard error of the mean. There is no significant difference in activity.

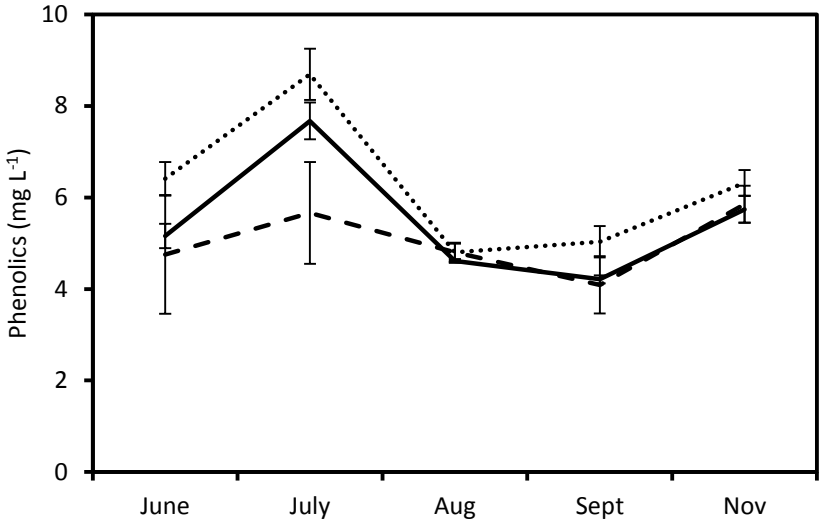

Figure 6. Mean phenolic concentrations (mg L^{-1}) for open control ditches (continuous line), reprofiled ditches (dotted line) and dammed ditches (dashed line) at Ffynnon Eidda during 2011. n=4 samples for each treatment. Errors bars show standard error of the mean. There is no significant difference in concentration.

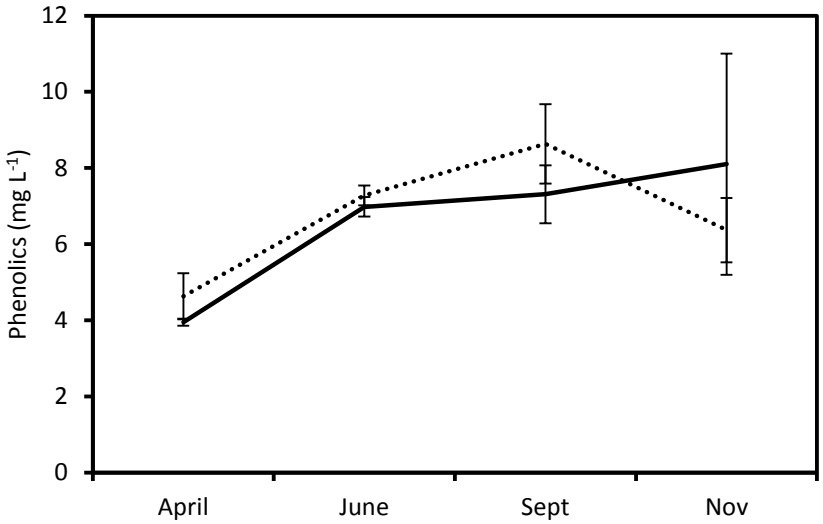

Figure 7. Mean phenolic concentrations (mg L^{-1}) open control (continuous line) and blocked ditches (dashed line) at Llyn Serw during 2010. n=4 for each value, except n=3 for the open ditch at Llyn Serw during June and September due to difficulty in obtaining samples. Errors bars show standard error of the mean. There is no significant difference in concentration.

4.3.2. Effect of ditch blocking on soil chemistry

At Ffynnon Eidda there was no treatment effect on pH. Mean values for the length of the study were 4.21 (open), 4.34 (dam) and 4.20 (reprofiled). Mean soil water content of samples was 90.7% (open), 89.2% (dam) and 88.1% (reprofiled). Repeated-measures ANOVA showed no significant difference in mean water content.

At Llyn Serw there was no significant difference in mean pH; 4.75 at the open ditch and 4.81 at the blocked ditch. Mean soil water content was 88.0% for the open ditch and 92.0% for the blocked ditch. Repeated-measures ANOVA showed this difference to be significant ($p<0.05$).

4.3.3. Site comparison – effect of long term drainage

Data from Bryn Du was used as an undrained control site, when sampling dates there coincided with those at Ffynnon Eidda and Llyn Serw. For Ffynnon Eidda this was the case in summer and autumn 2011. A comparison of the Bryn Du data with that from the open ditches at Ffynnon Eidda shows that the drained site had higher total hydrolase activity and phenol oxidase activity (figure 8). This result is similar for the two ditch blocking treatments at Ffynnon Eidda (figures 9 and 10). The hydrolase increase is primarily driven by significant enhancement of β-glucosidase activity in both months and by increased sulphatase

activity in September (table 2). In conjunction with this, Bryn Du displays a significantly higher phenolic concentration; 5.6 mg L^{-1} compared with 4.7 mg L^{-1} at Ffynnon Eidda, and a significantly higher pH; 4.27 compared to 4.18. There was no difference in the water content of soil samples (91.0% at Bryn Du, 90.7% at Ffynnon Eidda). However, mean sulphate concentrations were higher at Ffynnon Eidda (0.84 mg L^{-1} compared to 0.67 mg L^{-1}).

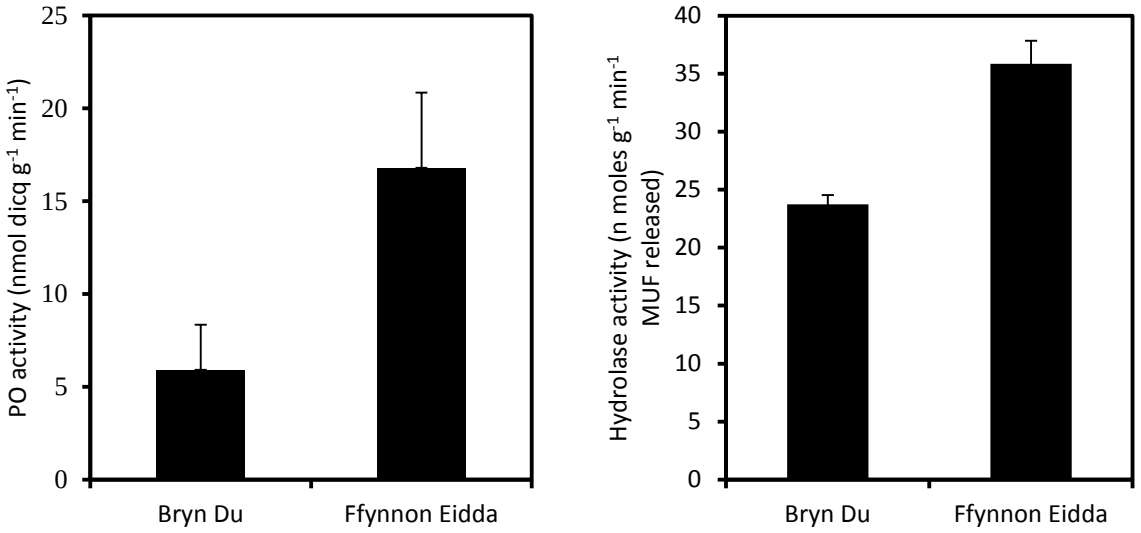

Figure 8. Mean phenol oxidase (PO) activity (nmol dicq g^{-1} min^{-1}) and total mean hydrolase activity (n moles g^{-1} min^{-1} MUF released) (i.e. sum of mean β-glucosidase, sulphatase, xylosidase and chitinase activity) at the undrained Bryn Du (control) and Ffynnon Eidda (drained) sites. Date is pooled from summer and autumn 2011. n=8 samples per treatment. Error bars show standard error of the mean. The difference is significant for phenol oxidase and hydrolases

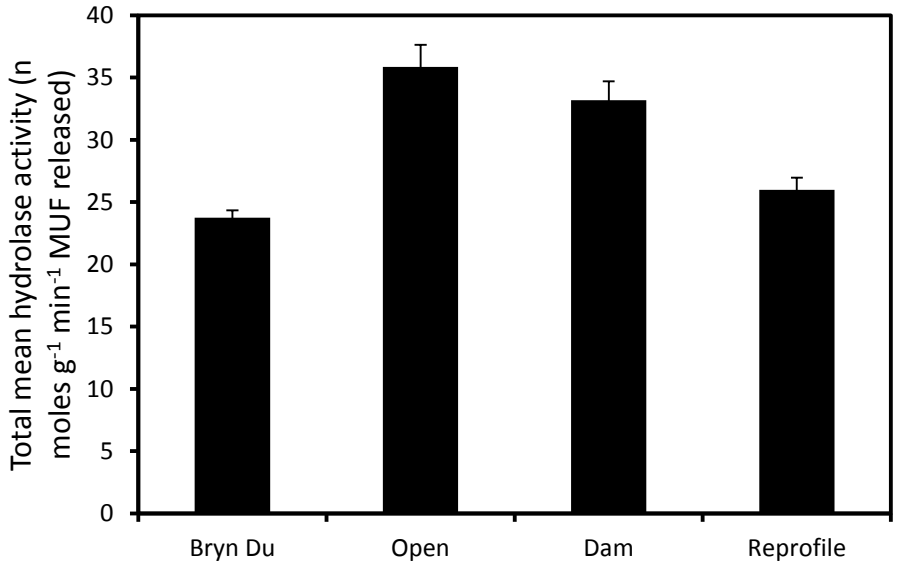

Figure 9. Total mean hydrolase activity (n moles g^{-1} min^{-1} MUF released) (i.e. sum of mean β-glucosidase, sulphatase, xylosidase and chitinase activity) at the undrained Bryn Du (control) site and

the three Ffynnon Eidda treatments: open ditches, dammed ditches, and reprofiled ditches. Date is pooled from summer and autumn 2011. n=8 samples per treatment. Error bars show standard error of the mean. The difference between Bryn Du and open ditches is significant.

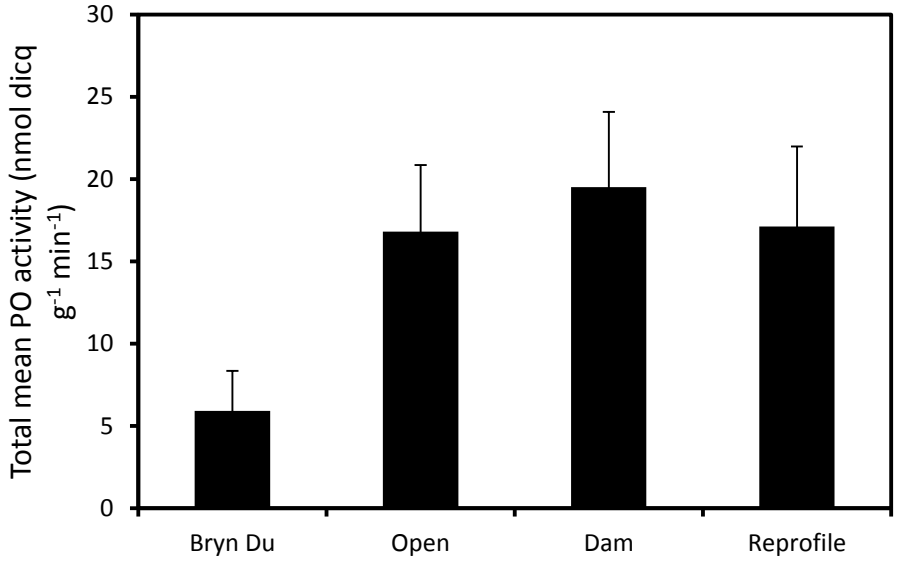

Figure 10. Mean phenol oxidase (PO) activity (nmol dicq g^{-1} min^{-1}) at the undrained Bryn Du (control) site and the three Ffynnon Eidda treatments: open ditches, dammed ditches, and reprofiled ditches. Date is pooled from summer and autumn 2011. n=8 samples per treatment. Error bars show standard error of the mean. The difference between Bryn Du and open, dammed and reprofiled ditches is significant.

Table 2. Mean hydrolase activites (n moles g^{-1} min^{-1} MUF released) and standard errors for β-glucosidase and sulphatase; the two hydrolase enzyme that showed significant differences between the drained Ffynnon Eidda site and the undrained Bryn Du site. For each month and enzyme n = 4.

	Bryn Du		Ffynnon Eidda	
	June	September	June	September
β-glucosidase	5.5	8.9	10.6	13.0
SE	1.06	0.86	2.97	1.26
Sulphatase	5.3	2.1	7.4	5.1
SE	0.94	0.58	1.50	1.11

For Llyn Serw there were two occasions when sampling at Bryn Du approximately coincided. These were summer and autumn 2010. During this period there was no significant difference in phenol oxidase activity but total hydrolase activity was lower at Llyn Serw (figure 11). The difference in total hydrolase activity was driven by differences in sulphatase and chitinase activity. There was no difference in phenolic concentrations (6.46 mg L^{-1} at Llyn Serw, 6.96 mg L^{-1} at Bryn Du) but Llyn Serw displayed a higher pH (4.44

compared to 4.27). Additionally, samples from Llyn Serw had lower mean water content (86.79% compared to 92.06). There was no significant difference in mean sulphate concentration (1.53 mg L-1 and 0.84 mg L-1 at Llyn Serw and Bryn Du respectively).

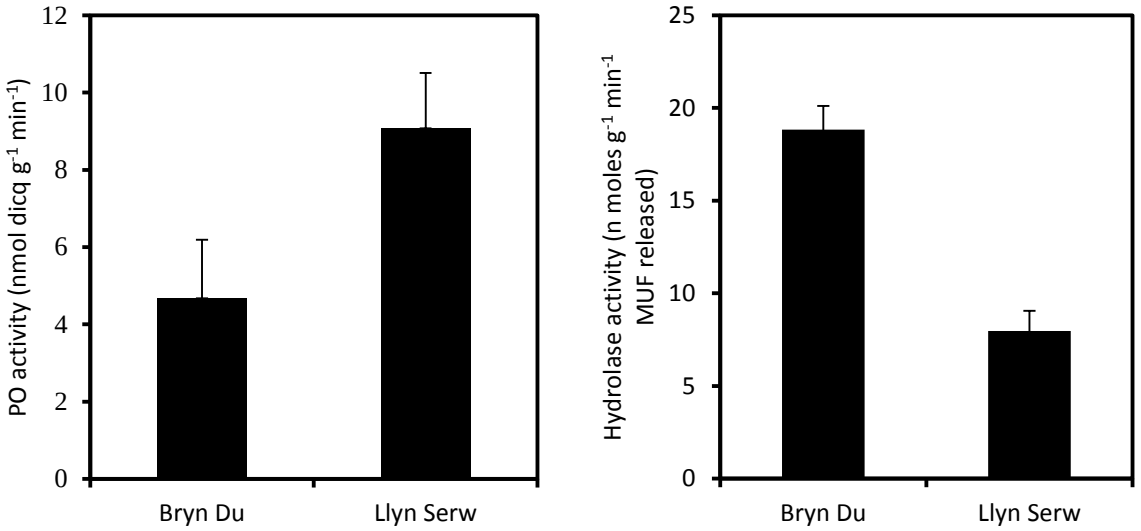

Figure 11. Mean phenol oxidase (PO) activity (nmol dicq g^{-1} min^{-1}) and total mean hydrolase activity (n moles g^{-1} min^{-1} MUF released) (i.e. sum of mean β-glucosidase, sulphatase, xylosidase and chitinase activity) at the undrained Bryn Du (control) and Llyn Serw (drained) sites. Data is pooled from summer and autumn 2010. n=8 samples per treatment. Error bars show standard error of the mean. The difference in phenol oxidase is not significant, but the difference in hydrolases is significant.

The ratio of phenolic to DOC concentrations and SUVA were used at each site as a basic proxy to examine the molecular weight of DOC. The mean values were 0.19 at Bryn Du, 0.18 at Ffynnon Eidda, and 0.12 at Llyn Serw. Mean SUVA values were 4.27 at Ffynnon Eidda, 4.42 at Bryn Du, and 3.24 at Llyn Serw.

4.4. Discussion

4.4.1. Effects of long term drainage

There were conflicting results from analysis examining the effects of long term drainage. Results from a comparison between an intact site (Bryn Du) and a drained site (open ditches at Ffynnon Eidda) support hypothesis 1; that drainage leads to lower phenolic concentrations, and enhanced activities of phenol oxidase and hydrolases. This is in accordance with Freeman *et al.* (2001a), who showed that increased oxygen availability following drainage stimulates phenol oxidase activity, which in turn degrades phenolics, and removes the inhibition on hydrolase enzymes. The enhancement of hydrolase activity was

primarily controlled by increased β-glucosidase activity, a response which has been observed before (Fenner *et al.*, 2005a).

A small difference in acidity was observed between the sites; pH at Ffynnon Eidda was lower than Bryn Du. It is probable that this difference was controlled by sulphate: drought events allow reduced sulphur compounds stored within the peat to be re-oxidised, resulting in the release of sulphate and hydrogen ions, which in turn lowers pH (Adamson *et al.*, 2001). In support of this, sulphate concentrations were higher at Ffynnon Eidda. Williams *et al.* (2000) found that for *Sphagnum* peat in north America, pH was the primary driver of phenol oxidase activity, and droughts had no effect. Although there was a significant difference in pH between Ffynnon Eidda and Bryn Du it was very small (0.09) and unlikely to have an influence on phenol oxidase activity. Additionally, long term drainage leads to greater water table fluctuations (Holden *et al.,* 2011) which can exacerbate the effects of seasonal drought, leading to an associated increase in oxygen availability of a magnitude to override pH controls and consequently stimulate phenol oxidase activity.

Droughts have been observed to reduce phenol oxidase activity, and it has been suggested that this is due to moisture stresses affecting the microbial production of phenol oxidase, or that it directly affects extracellular enzyme activity (Toberman *et al.* 2008b). Such a situation is different to that involving drainage. Samples from Ffynnon Eidda were taken from within the open ditches, which are still hydrologically active. As such, there was no difference in the water content of samples from Ffynnon Eidda and the undrained control site at Bryn Du. The ditches do have the ability to increase the aerobic zone, however, increasing oxygen availability to extracellular enzymes. As such, phenol oxidase activity may have been enhanced at the drained site due to the increased oxygen availability, without any detrimental moisture stress occurring.

Although data from drainage at Ffynnon Eidda strongly supports the literature, that from the second drained site at Llyn Serw is more complex, when compared to the undrained site at Bryn Du. There was no difference in phenol oxidase activity. Despite no observed difference in phenolic concentrations, hydrolase activity was lower at Llyn Serw, and this was associated with a higher pH, and samples with a lower water content. This is unexpected, as a more favourable pH and drier conditions would be expected to increase hydrolase activity (Fenner *et al.*, 2005a). The soil at Llyn Serw still possesses a high moisture content, and so it is unlikely that moisture stress on extracellular enzymes is a contributing factor, as Toberman *et al.* (2008b) found. It is also true that there are occasions where drought has not affected extracellular enzyme activity (Yavitt *et al.,* 2004). Whilst the

Ffynnon Eidda and Bryn Du sites are dominated by *Calluna*, the Llyn Serw site is situated in a large, shallow basin, and features *Calluna* plus large flushes of *Juncus* and *Eriophorum* where water drains into the lake. These plants could be supplying low-molecular weight root exudates to the soil (Saarnio *et al.*, 2004, Ström *et al.*, 2005), thus lessening the microbial demand for hydrolase enzymes (Sinsabaugh, 1994) that are usually responsible for the production of low molecular weight compounds such as glucose that are needed as an energy source by microorganisms. Litter type has been observed to control enzyme activity, even overriding the effects of water table (Straková *et al.*, 2011) and there is direct evidence in support of this hypothesis: the ratio of DOC:phenolics was similar at Ffynnon Eidda and Bryn Du, but was considerably lower at Llyn Serw. This is suggestive of DOC being composed of more low molecular weight compounds. Additionally, mean SUVA values were similar at Bryn Du and Ffynnon Eidda, but lower at Llyn Serw, and SUVA has been observed to correlate with molecular weight (Leenheer & Croué, 2003).

4.4.2. Effect of ditch blocking

At Ffynnon Eidda there was little evidence in support of hypothesis 2: that ditch blocking would suppress phenol oxidase activity, leading to a subsequent increase in phenolics and lowered hydrolase activities. Although hydrolase activities were consistently lower in the blocked ditches the only significance was for sulphatase, which was higher in the open ditches compared to the reprofiled ditches. The lack of observed differences for the other enzymes may in part be due to the small sample size. Data from this site was collected 4-9 months after blocking took place. Fenner & Freeman (2011) noted that upon rewetting after drought, phenol oxidase activity did not immediately decline, and remained high as a legacy from the previous aerobic conditions. Furthermore, the enzyme response was identical for the dammed ditches and the reprofiled ditches. It might be expected that activity would increase in the reprofiled ditches due to the severe disturbance that this method involves; large volumes of peat are removed from the adjacent borrow pits to infill the ditch, which theoretically would allow extensive oxygen infiltration. Clearly, this was not the case. Contrary to other studies, Toberman *et al.* (2008a) observed an increase in phenol oxidase activity in peat cores one week after drainage had been impeded. This rapid response was attributed to the action of submerging the cores in aerated stream water, followed by a later increase in pH. As pH had not responded to ditch blocking at Ffynnon Eidda, this change could not occur.

The suppression of sulphatase activity in the reprofiled ditches is likely to have repercussions on methane fluxes. Raising the water table will directly stimulate the methanogenic community and increase methane emissions (Komulainen *et al.*, 1998, Urbanová *et al.*, 2011). Coupled to this, sulphatase releases sulphate which is implicated in reduced methane emissions when the water table falls. The suppression of sulphatase following ditch blocking is likely to result in a reduced rate of sulphate production which will then contribute to the enhanced methane fluxes (Freeman *et al.*, 1997).

Although there has not yet been a site-wide recovery of the water table at Ffynnon Eidda following ditch blocking, water levels have been raised locally in relation to individual ditches, with large pools forming behind dams. Holden *et al.* (2011) suggest that ditch blocking only partially restores the hydrological functioning of blanket bog, and other evidence suggests that it could be several years before the rewetting finally suppresses enzyme activity (Fenner & Freeman, 2011). Other work has also shown no response in carbon-cycling enzymes upon rewetting, due to greater thermal stability and increased substrate availability after rewetting (Freeman *et al.*, 1998).

Results following ditch blocking at Llyn Serw were similar to those from Ffynnon Eidda; no difference was observed in hydrolase or phenol oxidase activity. At Llyn Serw, however, a significant difference was observed in soil water content, with samples from the blocked ditch being wetter. This is logical, as the recovery of the water table has been noted at Llyn Serw following ditch blocking (Cooper *et al.*, 2013). It might be that these hydrological changes are the precursor to future enzymatic changes, with expected associated alterations in biogeochemical cycling.

Finally, data from the two experimental sites (Ffynnon Eidda and Llyn Serw) can briefly be compared. A direct comparison is misleading, as data was collected during different years, and the thermal optimum for extracellular enzymes will potentially occur during different months (Fenner *et al.*, 2005b). Nevertheless, enzyme activities are consistently lower at Llyn Serw, and this provides further evidence for the presence of increased plant-derived low molecular weight root exudation there.

4.4.3. Conclusions

The data presented here provide conflicting information concerning the long term effects of peatland drainage on extracellular enzyme activities. Results from one site suggested that drainage had increased enzyme activity, but the results from a second site did not show this, possibly due to site difference in vegetation type, a result that Williams *et al.*

(2000) also found. These enzymes are implicated in the cycling of greenhouse gases (Kang *et al.*, 1998, Freeman *et al.*, 2001a) and DOC (Freeman *et al.*, 2001b) and so understanding their response to drainage can provide information on how gaseous and fluvial carbon cycling will change following drainage.

Following ditch blocking there was no evidence that enzyme activities were suppressed, even 27 months after rewetting. This was due to a legacy of enhanced activity that was originally stimulated through drainage. This supports results from Worrall *et al* (2007) who found that DOC increased one year after blocking. They attributed this to increased enzyme activities after drainage, which are then not suppressed immediately upon rewetting.

These results suggest that the response of extracellular enzymes to water table changes is complex, and that the relationship between hydrolase activites and phenolic concentrations is variable. In an additional complication, high enzyme activites are likely to have two contrasting effects on net DOC production: 1) high phenol oxidase activites will degrade phenolic compounds and, as phenolics are a type of DOC, lead to decreased DOC concentrations; 2) high hydrolase activites will enhance decomposition rates, thereby increasing DOC concentrations . It is clear that long term monitoring is necessary to elucidate exactly when peatland restoration will begin to influence the activity of extracellular enzymes, as changes can create both positive and negative feedbacks to ecosystem processes (Sinsabaugh, 2010). More substantial treatment effects following drainage and rewetting may have been obscured as enzyme activity varies over spatial scales according to local changes in pH, hydrology and vegetation. Future work should drastically increase sample sizes on both temporal and spatial scales, as well as including the collection of replicated samples for analysis. Such an approach might lead to a better understanding of extracellular enzyme responses to ecosystem changes.

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The short-term effect of ditch blocking on dissolved organic carbon concentrations

5.1 Introduction

Dissolved organic carbon (DOC) is a fluvial export from peatland catchments. Its concentration is affected by various factors, including soil carbon pool, peat cover (Aitkenhead *et al.*, 1999), hydrology (Dawson *et al.*, 2004), and vegetation (Palmer *et al.*, 2001, Armstrong *et al.*, 2012), and it is also influenced by environmental changes such as atmospheric deposition (Monteith *et al.*, 2007, Evans *et al.*, 2012), climate (Freeman *et al.*, 2001b), rising carbon dioxide concentrations (Freeman *et al.*, 2004) and land use (Clutterbuck & Yallop, 2010). There is growing concern for human health due to the formation of harmful disinfectant by-products (such as trihalomethanes) when water with a high DOC concentration is chlorinated for drinking supplies (Chow *et al.*, 2003), and high levels of DOC result in increased treatment expenditure by water companies due to the use of a higher coagulant dose, increased filter backwashing, and the production of larger amounts of sludge (McDonald *et al.*, 1991). Furthermore, DOC can affect the functioning of aquatic ecosystems (Karlsson *et al.*, 2009), and is a significant component of the global carbon cycle as it is mineralised to carbon dioxide and returned to the atmosphere (Hedges *et al.*, 1997, Cole *et al.*, 2007, Bianchi, 2011)

In the UK there has been a long history of drainage, with the aim of improving the land for grazing, shooting, and forestry. This is carried out through the digging of ditches which are typically spaced every 15 m on blanket bog (Stewart & Lance, 1991). These ditches may be enhancing DOC exports. By increasing the extent of the aerobic zone a large store of microbially-generated DOC is produced (Mitchell, 1991, Waddington *et al.*, 2008). Sachse *et al.* (2005) analysed a variety of water samples to investigate the influence of catchment characteristics and recorded the highest DOC concentrations and humic substances in fen ditch water. Wallage *et al.* (2006) found evidence suggesting that drainage had lowered the water table and increased microbial activity to a depth of 20 cm, with a resultant increase in DOC production. Extreme drying causes macropores to collapse and creates hydrophobic compounds thus hindering complete rewetting (Mitchell, 1991). Following drought, rewetting then leads to the export of this DOC store (Fenner & Freeman, 2011). In UK peatlands this cycle occurs when a summer drought is followed by a wetter autumn, leading to an 'autumn flush' of DOC (Mitchell & McDonald, 1992). It is also seen to generally occur at other times of the year, whenever a dry month precedes a wet month

(Mitchell & McDonald, 1995, Toberman *et al.*, 2008). For particularly severe droughts this flush will not occur until the next autumn, as the first period of rewetting is insufficient to remove the seasonally-generated DOC store (Mitchell & McDonald, 1992). It has also been shown that the clearing of old ditches increases DOC concentration, as areas of bare peat are exposed to weathering, therefore providing a fresh source of organic material (Baker *et al.*, 2008).

Considering this, it is not unreasonable to postulate that ditch blocking might be an appropriate management technique to regulate DOC concentrations in peatlands. It would first be expected that raising the water table through restoration would lead to a flush of DOC out of the system. Added to this, many restoration techniques (including ditch blocking) use mechanical intervention and can be quite destructive. For example, peat is mechanically dug from areas beside ditches to provide substrate for ditch dams, leaving depressions known as 'borrow pits' that fill with water. The bases of the ditches are sometimes compressed, with the aim of destroying soil pipes to restrict their hydrological functioning. As 'ecosystem disturbance' has been shown to enhance DOC concentrations (Glatzel *et al.*, 2003) it might be assumed that the restoration work would directly impact upon DOC cycling in the short term. In support of this hypothesis, Worrall *et al.* (2007a) found that DOC concentrations approximately doubled in the year following blocking. They attributed the increase to DOC flushing or the delayed suppression of extracellular enzymes that had been activated by the favourable conditions of the previously lowered water tables; a mechanism demonstrated by Fenner & Freeman following drought (2011).

The short-term and long-term responses to restoration may not be the same. On a blanket bog where ditches had been blocked six years previously, Wallage *et al.* (2006) found that pore water DOC concentrations were 60-70% lower compared to a nearby drained area, as well as being lower than a nearby intact site. Modelling by Worrall *et al.* (2007b) predicted that ditch blocking could reduce DOC exports, though this was dependent on the spacing between ditches. However, the model did not factor in the influence of slope on hydrology, and assumed that a blocked catchment reverts to DOC leaching levels equivalent to an intact site. As described previously, this may not be true in the short to medium term.

A UK-wide survey of thirty-two sites showed significantly lower DOC concentrations in blocked ditches. However, the same paper also reported on an intensively monitored site where no difference in DOC flux or concentration was found seven years after blocking (Armstrong *et al.*, 2010). There is a caveat with regards to the intensive study: rainfall was 1.85 m per year and yet if the runoff is calculated (using water flux and catchment size)

values are reached of 3.46 m yr^{-1} (blocked catchment) and 3.12 m yr^{-1} (unblocked catchment). This discrepancy could either be due to difficulties in accurately measuring flow, or in defining the catchment of the ditches, but as water outflows considerably exceed rainfall then the accuracy of the calculated DOC exports is questionable.

Gibson *et al.* (2009) noted a significant decrease in DOC concentration after ditch blocking, but only by a mean of 0.3 mg L^{-1}. The authors argue that DOC production in all peat is uniform, and that DOC export is controlled by hydrology. Consequently, a reduction in DOC flux due to a decrease in measured runoff in blocked ditches was recorded. For this mechanism to reduce DOC loss, however, it is necessary either that there is a decrease in total water flux from the site (i.e. an increase in evapotranspiration) or that water leaving the catchment in unmeasured subsurface flow contains lower DOC concentrations (for example if this water passed through a DOC-retaining mineral horizon). In a high rainfall blanket bog, however, neither mechanism appears likely. The work of Gibson *et al.* (2009) also raises the point that ditch blocking studies can be confounded by the effects of catchment size on DOC exports because larger catchments are more likely to have areas of mineral soil, and will have increased potential for in-stream DOC removal. This should therefore be considered if blocked and control ditches are in different catchments.

Another study found that ditch blocking slightly raised DOC concentrations. After one year DOC concentrations from ditches then decreased markedly, but increased in streams. Another observation of the study was that instantaneous yields (i.e. flow-weighted) of DOC in streams declined sharply after rewetting (Wilson *et al.*, 2011a). This would be expected as blocking disrupts water flow. The paper does not report numerous essential data such as catchment sizes, making it impossible to accurately duplicate their analysis. Nevertheless, it is difficult to reconcile the stated DOC fluxes of 0.48 g m^{-2} yr^{-1}(blocked) and 4.07 g m^{-2} yr^{-1} (unblocked) with DOC concentrations of approximately 22 mg L^{-1} (stream-blocked) and 20 mg L^{-1} (stream-unblocked). These figures would give unrealistic low flows of 0.022 m yr^{-1} and 0.204 m yr^{-1}, and are suggestive of basic discharge measurement errors. As in Gibson *et al.* (2009) the authors describe the ditch blocking as successful for lowering DOC exports only on the basis of reduced flow in blocked ditches. Like Armstrong *et al.* (2010) this suggests an inherent difficulty in accurately quantifying flows. As such, it may be that differences in DOC concentrations, rather than fluxes, are more reliable indicators of restoration success in high-rainfall systems, such as blanket bogs.

These studies claiming that ditch blocking reduces water flow and therefore DOC export are perhaps not considering the entire picture. It has been suggested that an increase

in evapotranspiration after blocking could not complete the water budget (Gibson *et al.*, 2009). The evapotranspiration rate for two Welsh moorland catchments varied between 16-25% of rainfall depending on the extent of forest cover (Institute of Hydrology, 1976), and drainage should result in decreased evapotranspiration (Richardson, 1983, Holden *et al.*, 2004). Most studies of drained peats have focused on harvested sites, with reductions in evapotranspiration after drainage being measured in two studies as 26% and 30% (Richardson & McCarthy, 1994, Ledger & Harper, 1987). However, these studies involved drained sites where the removal of peat and vegetation had also occurred. Where sites have solely been ditched the reduction is likely to be less, and thus increased evapotranspiration after ditch blocking is unlikely to result in the large declines in fluxes necessary to produce the lowered DOC exports reported by Wilson *et al.* (2011a). An obvious candidate to fill the gap in the water budget is therefore overland flow. Holden *et al.* (2006) found overland flow to occur more frequently in an intact catchment compared to a drained catchment, with the intact catchments displaying very little runoff below a depth of 10 cm, and that overland flow occurred only at saturated areas. Wilson *et al.* (2011b) measured an increase in occurrence of overland flow after ditch blocking. This mechanism may also be promoted by the restoration techniques that are used; some methods of ditch blocking create dams to hold back water flow, and it is common practice to dig overflow channels round the side of the dams. These funnel excess water out of the ditches. Theoretically, ditch blocking would therefore reduce water flux down the ditch line, but increase water flux overland. Wallage *et al.* (2006) recorded a median DOC value of 8.53 mg L^{-1} from overland flow, lower than pore water measurements. More data are needed to observe the range of DOC concentrations in overland flow; it may not always be low.

Turner *et al.* (2013) presented results from an experiment with a one year pre-blocking control period, using a control catchment and a treatment catchment where ditches were then blocked. They measured a decrease in ditch DOC concentration of 2.5% in the year following ditch blocking, a similar result to that of Gibson *et al.* (2009). Turner *et al.* (2013) also noted a reduction in ditch water flux after blocking with an associated decrease in DOC export. However, this reduction in DOC export was larger in zero order ditches than first order ditches (i.e. the magnitude of the reduction decreased moving down slope) and the authors hypothesised that the ditch dams were diverting water out of the ditches as "bypass flow", or that other external water sources were contributing dilution effects at different ditch scales.

There is a dearth of information on the long-term effects of restoration but Höll *et al.* (2009) found lower DOC concentrations twenty years after rewetting compared to a moderately drained fen. They stressed the importance of maintaining a stable, shallow water table during periods of high biological activity so as to regulate DOC concentrations. McDonald *et al.* (1991) reinforce this point by noting that it is the movement between wet and dry phases that generates DOC.

Another fluvial export of carbon is particulate organic carbon (POC). POC exports are not considerably lower than DOC exports, but it is often not included in sampling programs (Holden, 2005). Peatland drainage has been shown to directly increase POC concentrations (Ahtiainen & Huttunen, 1999, Ramchunder *et al.*, 2012). Drainage also leads to an increase in the density and size of soil pipes, and the rate of pipe erosion increases exponentially over time enhancing POC losses (Holden, 2006). After ditch blocking Wilson *et al.* (2001a) noted no change in POC concentrations but decreased POC exports. They concluded that the pools that formed behind dams allowed POC to settle out. An earlier survey by Holden *et al.* (2007) found lower POC yields associated with blocked ditches compared to open ditches.

It can be concluded that there are two primary shortcomings of many of the ditch blocking experiments that have taken place so far: 1) some studies only have data taken after ditch blocking, with no pre-blocking baseline data, 2) some studies have blocked and unblocked ditches that are geographically separated, which may result in subtle but important differences in hydrology, vegetation, gradient, soil, and catchment size, all of which can affect DOC concentrations. This study therefore aims to rectify these shortcomings by using a replicated, pre- and post-blocking design to test the effects of ditch blocking on DOC concentrations.

5.2. Materials and Methods

5.2.1. Study sites

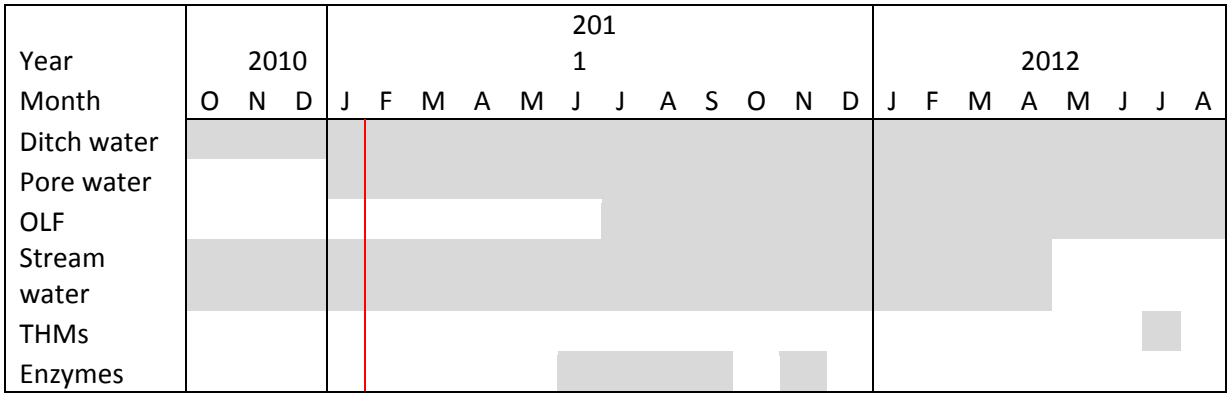
The study was carried out at the head of the Afon Ddu catchment (latitude 52.97°N, longitude 3.84°W) on the Migneint blanket bog, in Snowdonia National Park, north Wales (UK). The altitude of the catchment ranges from 460-510 m with a mean peat depth of 1.32 m. Dominant vegetation is *Calluna vulgaris* with some *Eriophorum* and *Sphagnum* species. For the purpose of this study a catchment of 1.59 km^2 was defined. The total length of ditches within the catchment was estimated at 32.5 km.

The experimental part of the site comprises twelve adjacent ditches that run directly downslope in a north-northwest direction (fig. 1). The ditch spacing is 10-20 m. Ditch blocking throughout the catchment took place in February 2011. At the experimental part of the site, four ditches were left open as controls, and eight were blocked using two different methods. Four were blocked using peat dams, whereby the peat is extracted from 'borrow pits' adjacent to the ditch. The remaining four were blocked using a reprofiling technique. This involves the ditch vegetation being removed, and the peat bottom being compressed to destroy any natural pipes that may be present and hydrologically active. The ditch is then infilled with peat and the vegetation is replaced. As in the previous treatment peat dams are also constructed along the ditch. At all dams small channels were created to funnel water out of the ditch line. The purpose of this is to shed water onto the peat surface with the aim of it infiltrating more evenly across the bog, rather than following the original drainage line. For the rest of the catchment all ditches were blocked using the reprofiling technique.

The experimental ditches were assigned their respective treatment (control, dammed, reprofiled) according to a randomised design, to minimise the potential influence of any linear change across the hill slope (such as peat depth). Ditches were grouped using flow rate, i.e. the three ditches with lowest flows were each assigned a different treatment, the three with largest flows were each assigned a different treatment, and so forth.

A second site was used as an unblocked control catchment. The Nant y Brwyn is 2.5 km away from the Afon Ddu, and is also part of the Migneint blanket bog (fig. 2). Its site characteristics are similar to that of the Afon Ddu catchment: altitude ranges 400-490 m with mean peat depth of 1.17 m. Dominant vegetation is *Calluna vulgaris* with some *Eriophorum* and *Sphagnum* species. For the study a catchment of 1.57 km^2 was used (Cooper, 2013). The total open ditch length within the catchment was estimated at 25.7 km.

Table 1. Timeline of when different measurements were taken throughout the study. OLF = overland flow, THMs = trihalomethanes.



5.2.2. Water sampling

Water sampling in the Afon Ddu catchment took place on an approximate monthly basis for three different samples types. Sampling of ditch waters commenced in October 2010 with samples being taken directly from water flowing in the ditch. This gave three sets of pre-blocking data for ditch water. Pore water sample collection commenced in January 2011 and samples were taken from piezometers at 15 cm depth. Groups of two or three piezometers were situated together 2 m to the west of each ditch. Water samples from each group of piezometers were bulked together for analysis. This gave one set of pre-blocking data for pore water. Overland flow (OLF) water sample collection started in July 2011, after ditch blocking had taken place. Samples were taken from crest-stage tubes (CSTs); polypropylene tubes sealed at both ends, featuring holes slightly above ground level to collect overland flow. CSTs were situated in groups of two or three, and were located 2 m and 4 m either side of each ditch. OLF samples were bulked together from each group of CSTs. Due to fluctuating water tables it was not always possible to collect a full set of piezometer and OLF water samples. Samples used for this study were collected up to the end of October 2012.

To compare changes in DOC concentration at the catchment scale, water samples were taken from the stream draining the experimental catchment (Afon Ddu) and the stream draining the unblocked, control catchment (Nant y Brwyn). Samples were taken approximately monthly from January 2007 to April 2012, as part of the Centre for Ecology and Hydrology (CEH) Carbon Catchment monitoring programme (Burden et al., in prep). After collection all samples were stored in the dark at 4^{o}C until analysis.

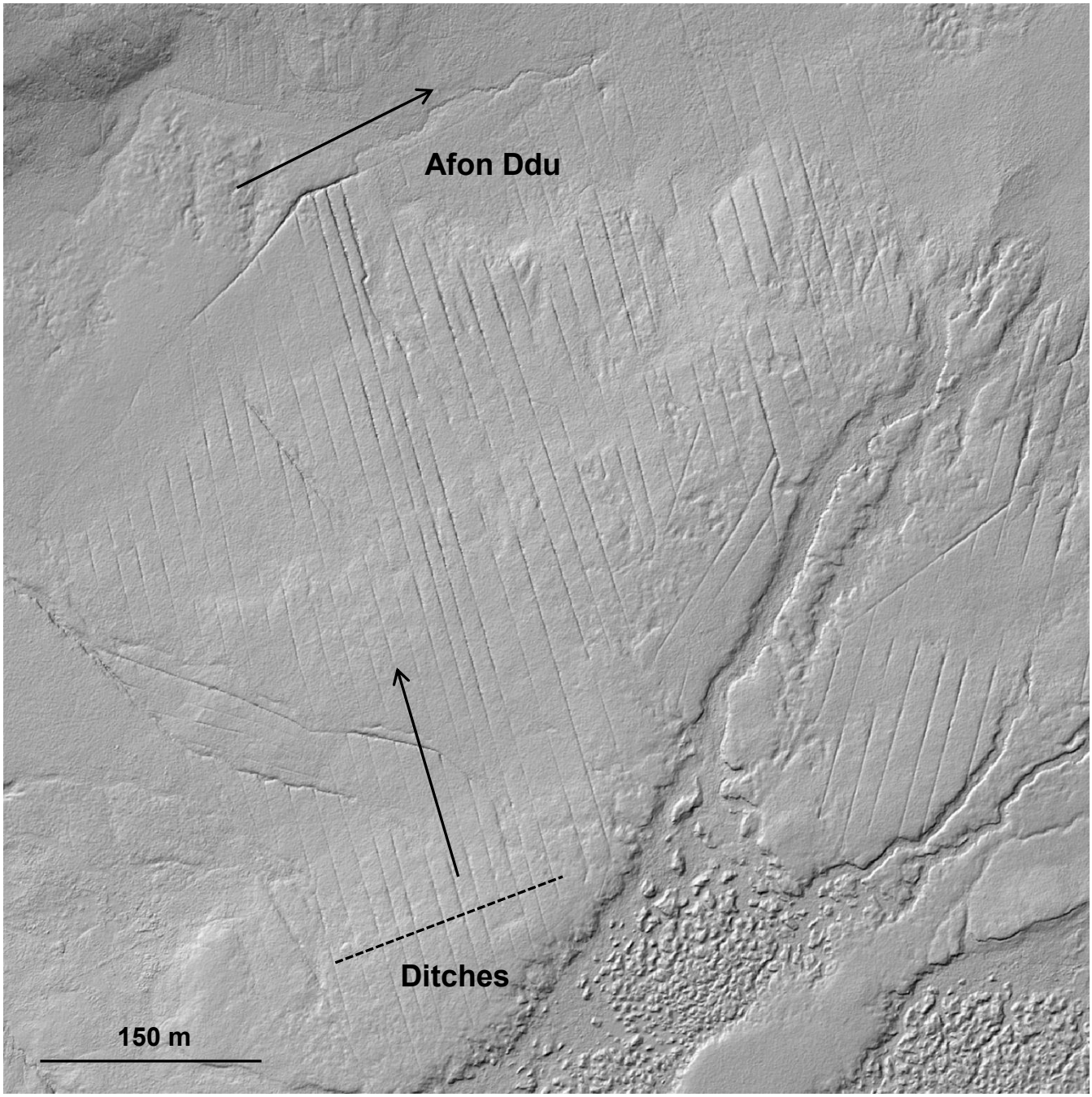


Figure 1. LIDAR image of the experimental ditches in Afon Ddu catchment, taken before ditch blocking. Dashed line indicates the 12 experimental ditches where ditch water, pore water, and OLF was sampled from. Ditches drain down slope according to the arrow, and into the Afon Ddu stream. Afon Ddu stream samples were taken further down (see figure 2). North is directly up.

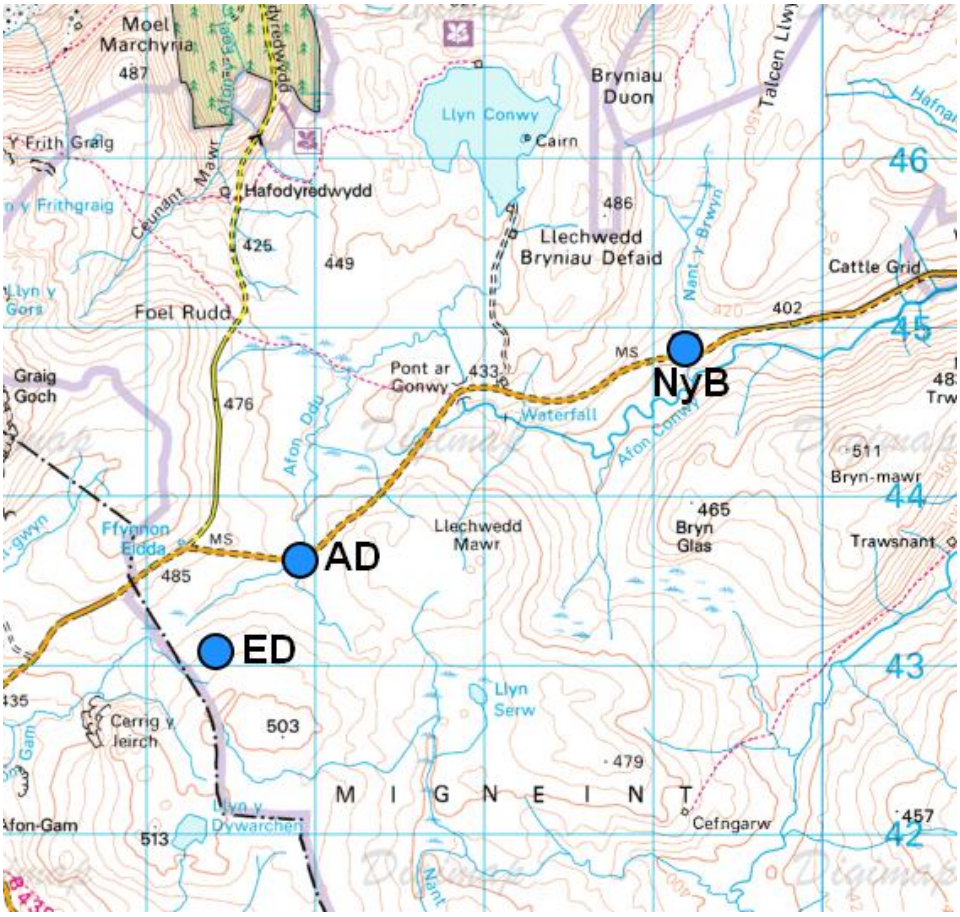


Figure 2. Map showing the sampling locations for streams draining the Afon Ddu catchment (AD) and Nant y Brwyn catchment (NyB) where stream samples were taken from. The location of experimental ditches (ED) from figure 1 is marked, where ditch water, pore water and OLF was sampled. Each grid square is 1 km by 1 km. North is directly up. © Crown Copyright/database right 2012. An Ordnance Survey/EDINA supplied service.

5.2.3. Water chemistry analysis

Electrical conductivity (EC) was determined on unfiltered samples using a calibrated (KCl standards) Jenway 4320 conductivity meter. Analytical grade standards were analysed at regular intervals to check instrumental drift. pH on unfiltered samples was analysed by titration using a 0.01N H_2SO_4 solution on a Metrohm 888 Titrando (2 buffer standards, pH 4 and 7). To determine POC, 500 mL of deionised water was passed through Whatman GF/C filters, which were then placed in a furnace at 550 ^{o}C for three hours, and the mass determined once cooled. Using the same filters, 500 mL of sample was passed through and the filters dried for 3 hours at 105 ^{o}C, allowed to cool and the mass recorded. The filters were placed in the furnace for a further three hours at 550 ^{o}C, and mass noted once cooled. The mass difference between the last two furnace phases provides the mass of particulate

organic matter, of which it is assumed that 50% of the mass is particulate organic carbon (Francis, 1990).

DOC was analysed as non-purgeable organic carbon. Samples were filtered through Whatman 0.45 μm cellulose nitrate filters and analysed using an Analytical Sciences Thermalox Total Carbon analyser. Samples were acidified (pH < 3) and sparged with oxygen to remove any inorganic carbon, and DOC concentrations calculated using a seven point calibration curve (plus a quality control sample), with additional standards to check for drift, and several samples (1-3 per run) duplicated to check for reproducibility. Each individual sample was injected 5 times, and the result accepted if the coefficient of variation of the five injections was less than 3%.

Sulphate concentrations were determined using either a Dionex DX-120 Ion Chromatograph with AS40 Autosampler, using a seven point calibration of analytical standards, or using a Metrohm 850 Professional IC with 858 Professional Sample Processor with a five point calibration of analytical standards.

Stream samples collected from the Afon Ddu and Nant y Brwyn catchments were analysed using comparable methods at the CEH Central Laboratory, Lancaster.

5.2.4. UV-vis analysis

Light absorbance of water samples was measured to give information on the molecular composition of DOC. UV-vis absorbance was measured using a Molecular Devices M2e Spectramax plate-reader. Wavelengths were scanned on a 1 nm increment from 230 nm to 800 nm, and results were corrected against blanks of ultrapure water. Of interest to the study were the E2:E3 ratio (absorbance at 250:365 nm), E2:E4 ratio (250:400 nm), E4:E6 ratio (465nm:665nm) and SUVA (specific ultraviolet absorption, which normalises absorbance at 254 nm to DOC concentration). These measurements are used as proxies for aromaticity (E2:E3) (Peuravuori & Pihlaja, 1997), humification/ratio of colourless to coloured DOC (E2:E4) (Park *et al.*, 1999, Selberg *et al.*, 2011, Graham *et al.*, 2012), humification (E4:E6) (Thurman, 1985, Summers *et al.*, 1987) and aromaticity (SUVA) (Weishaar *et al.*, 2003). All ditch water samples were analysed except one set from May 2012, due to a technical error with the Spectramax. All pore water samples were analysed except sets from May 2012 and early August 2012. OLF samples were analysed for dates from January to October 2012, with the exception of samples from May and early August 2012.

5.2.5. Trihalomethane formation potential (THMFP)

To simulate the formation of harmful trihalomethanes (THMs) during water treatment, and any effect rewetting might have upon them, one set of ditch water samples from July 2012 was analysed for THMFP, using the method of Gough *et al.* (2012). Samples were diluted to 1 mg L^{-1} DOC to provide standardised values. 2.0 mL of 0.5 M KH_2PO_4 was added to 97.5 mL of diluted sample to buffer the solution to a pH of 6.8. 0.5 mL of NaOCl was then added to provide 5 mg of free Cl per mg of DOC. After a seven day darkened incubation period at 25^{o}C, 0.4 mL of 0.8 M Na_2SO_3 was used to quench the reaction. Extraction of THMs was performed using direct immersion solid-phase microextraction (SPME) and quantified on a Varian 450 gas chromatograph coupled with an electron capture detector.

5.2.6. Extracellular enzyme analysis

Soil samples were taken from ditches and the areas between ditches at 10 cm depth during 2011. Phenol oxidase activity was measured using a method modified from Pind *et al* (1994). A small amount of soil (approximately 1 cm^3) was weighed and combined with 9 ml of ultra-pure water in a stomacher bag. This was homogenized for 30 seconds using a Seward Stomacher 80. Six replicates of 750 µl of homogenate were extracted into centrifuge vials; of these, 750 µl of ultra-pure water was added to three replicates (as blanks), and 750 µl of 10 mM L-DOPA (L-3,4-dihydroxyphenylalanine) (Sigma-Aldrich) was added to the other three. Samples were then left at field temperature for 9 minutes, before being centrifuged at 10,000 rpm for 5 minutes to terminate the reaction. 300 µl of supernatant was then transferred to a microplate and absorbance measured at 460 nm using a Molecular Devices M2e Spectramax plate-reader. The mean absorbance of the three blank replicates was subtracted from the mean absorbance of the three L-DOPA replicates, and phenol oxidase activity calculated according to the Beer-Lambert Law and the molar absorption coefficient for phenol oxidase (37000). As in Toberman *et al* (2008a) no pH buffer was used so as to simulate field conditions as accurately as possible.

Analysis of β-glucosidase activity was measured using a method modified from Freeman *et al* (1995). Soil samples were homogenized as for the phenol oxidase analysis, although 7ml of MUF-β-D-glucoside substrate was used in place of ultra-pure water, at 400 µM concentration. After homogenization, stomacher bags were incubated at field temperature for 60 minutes, and 1.5 ml of homogenate was transferred to a centrifuge vial before centrifuging for 5 minutes at 10,000 rpm. 300 µl of supernatant was extracted onto a

microplate. Standard curves were prepared using 0-40 μM MUF-free acid and soil samples, to correct for the quenching effect of phenolics. Fluorescence was measured at 450 nm emission and 330 nm excitation with a slit setting of 2.5 nm, using a Molecular Devices M2e Spectramax plate-reader.

5.2.7. Statistical analysis

Statistical analysis was performed using SPSS v20 (IBM Corporation, http://www-01.ibm.com/software/analytics/spss/products/statistics/). After testing for normality, ANOVAs or repeated measures ANOVAs were used to investigate differences between control ditches and the two different ditch blocking methods. As samples could not always be collected from piezometers and CSTs some data were missing. To solve this problem, OLF data from the four samples adjacent to each ditch were combined to give one mean value per ditch. For pore waters this problem was solved by the use of a mixed model ANOVA with a scaled identity covariance structure matrix, with treatment as a fixed effect and sampling date as a random effect (as in Wills *et al.,* 2006, Maynard *et al.,* 2011). T-tests were used to test for differences between the two years. For analysis of ditch and piezometer samples, pre- rewetting data were available, and therefore samples were grouped into those taken before ditch blocking took place, and those taken after blocking. This is important; if a statistical difference is already present before ditch blocking, then any significant difference after ditch blocking may be coincidental, and not due to the restoration work. The small pre-rewetting sample sizes will limit the power of any tests, however. Linear regression was used to test for relationships between water samples types (ditch, pore and OLF) and for enzyme analysis.

5.3. Results

5.3.1. Basic water chemistry

Table 2 displays mean pH and electrical conductivity for ditch samples, piezometer samples, and overland flow samples. OLF samples showed the largest variation for pH and EC, but the largest range for sulphate occurred in pore waters (though note that only limited data were available for sulphate in OLF). For all three samples types there was no significant difference between treatments for pH, EC or sulphate concentration.

Table 2. Mean pH, electrical conductivity (EC) (in µS/cm) and sulphate concentration (in mg SO_4^{2-} L^{-1}) data for water samples from ditches, piezometers, and overland flow. SE is the standard error of the mean. For pH and EC *n* = 108 for each treatment for ditch samples, and *n* = 76 for sulphate, except *n* = 81 for dam pH samples (see appendix). For pH piezometer samples *n* = 92, 95 and 87 for control, reprofile and dam treatments respectively, for EC samples *n* = 91, 92 and 85, and for sulphate *n* = 39 for control and reprofile treatments, and 37 for dammed. For OLF samples pH and EC *n* = 139, 137 and 129 for control, reprofile and dam treatments respectively, and for sulphate *n* = 16.

		Ditch		Pore		OLF	
		Mean	SE	Mean	SE	Mean	SE
pH	Control	4.24	0.01	4.13	0.02	5.11	0.08
	Reprofile	4.22	0.01	4.11	0.01	5.31	0.08
	Dam	4.28	0.02	4.13	0.02	5.48	0.09
EC	Control	42.8	1.37	57.4	1.17	37.6	0.99
	Reprofile	44.6	1.39	57.4	1.4	44.5	3.15
	Dam	40.5	1.36	58.4	1.71	50.5	4.37
SO_4^{2-}	Control	1.13	0.11	1.86	0.38	1.18	0.13
	Reprofile	1.15	0.09	1.54	0.26	1.29	0.12
	Dam	1.11	0.08	2.21	0.37	1.15	0.12

5.3.2. Ditch waters

There was no significant effect of either ditch blocking method on DOC concentration (fig. 3). Mean concentrations were 24.0 mg L^{-1}, 26.6 mg L^{-1}, and 24.5 mg L^{-1} for the control, reprofiled and dammed ditches respectively. Highest observed concentrations occurred in July 2011 with a mean peak (across all 12 ditches) of 48.6 mg L^{-1}, and lowest concentrations occurred in October 2012 (mean of 8.6 mg L^{-1}). There was no significant difference in total mean DOC concentration between the two years (measured as October 2010 - September 2011, and October 2011 - September 2012). A lack of treatment effect is reinforced by a comparison of water samples taken from the stream (Afon Ddu) draining the experimental catchment and from the stream (Nant y Brwyn) draining the control catchment where ditches have not been blocked (fig. 4). Mean DOC concentrations since ditch blocking were 10.5 mg L^{-1} at the Afon Ddu and 9.2 mg L^{-1} at the Nant y Brwyn. As *n* = 1 for each stream no statistical comparison can be used, but a visual comparison is useful. Each year there is a peak in DOC concentration in late summer, and for every occasion except 2007 this peak is larger in the Afon Ddu. For most years the difference is negligible, but for 2011 it was 14.7 mg L^{-1}. A regression analysis of the paired data from the two catchments shows that this

peak in the Afon Ddu is far removed from the trend line, and is therefore deviating from the expected concentration based on previous years (fig. 5). DOC concentrations were generally lower in the streams than the ditches. The largest peak in stream DOC occurred in August 2010 when concentrations were 27.1 mg L-1 at the Afon Ddu and 25.5 mg L-1 at the Nant y Brwyn. Lowest concentrations of 3.2 mg L^{-1} and 3.7 mg L^{-1} respectively were observed in January 2012.

UV-vis analysis showed that there was no significant difference in any of the four measures of DOC quality (fig. 6) between each treatment. As such, total means when all treatments were combined were: E2:E3 = 3.6, E2:E4 = 6.3, E4:E6 = 6.0, SUVA = 4.7. After chlorination and a seven day incubation, two species of THM were detected in ditch water samples from July 2012. These were chloroform ($CHCl_3$) and dichlorobromomethane ($CHBrCl_2$). ANOVA showed no significant difference in THMFP (fig. 7), and combined mean STHMFP was 148 μg THM / mg DOC.

Repeated measures ANOVA showed no significant difference in POC concentrations (fig. 8), but concentrations for all three treatments were extremely variable and showed large fluctuations. Mean concentrations for control, reprofiled and dammed ditches were 1.5 mg L^{-1}, 2.1 mg L^{-1}, and 2.4 mg L^{-1}, and respective ranges were 0-11.3 mg L^{-1}, 0.1-15.7 mg L^{-1}, and 0.1-41.1 mg L^{-1}. There was a suggestion that POC was generally higher in blocked ditches: for reprofiled and dammed treatments there were 36 and 38 samples respectively that showed concentrations 1-5 mg L^{-1}, compared to 31 samples for open ditches. The number of samples with concentrations 5-10 mg L^{-1} was 8 for each of the blocked treatments but 3 for open ditches, and for concentrations > 10 mg L-1 there were 4 and 6 samples for reprofiled and dammed treatments, and 3 for open ditches. There was no significant difference in POC concentration between the two years of data.

ANOVA showed no significant difference in the activity of phenol oxidase or β-glucosidase (fig. 9) during summer and autumn 2011. Total means were 16.4 n mol dicq g^{-1} min^{-1} for phenol oxidase and 8.0 n moles g^{-1} min^{-1} MUF released for β-glucosidase. There was a significant inverse relationship between β-glucosidase activity and DOC (fig. 10) concentration, but no relationship between phenol oxidase activity and DOC.

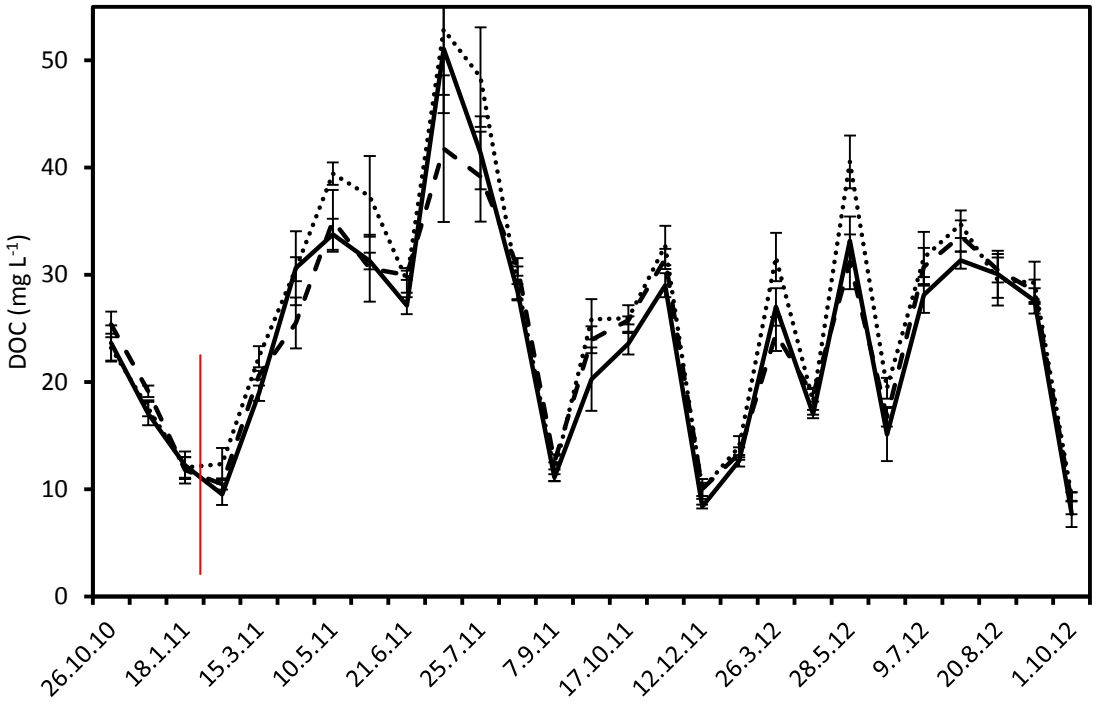


Figure 3. Monthly mean ditch DOC concentrations for open control ditches (continuous line), reprofiled ditches (dotted line) and dammed ditches (dashed line). n = 4 for each treatment (see appendix for cases where this is not true). Error bars show standard error of the mean. Red line indicates when ditch blocking occurred. There is no significant difference between treatments.

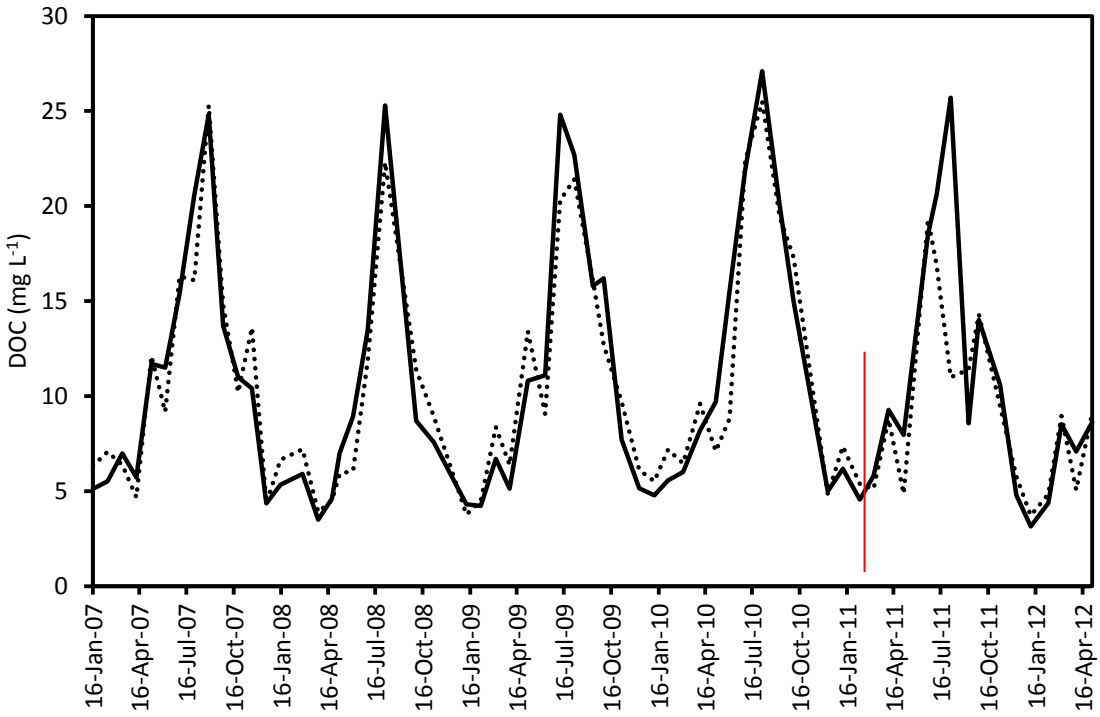


Figure 4. Monthly DOC concentrations for a stream draining the ditch blocked catchment (Afon Ddu, continuous line) and a control unblocked catchment (Nant y Brwyn, dotted line). Red line indicates when ditch blocking took place in the Afon Ddu catchment.

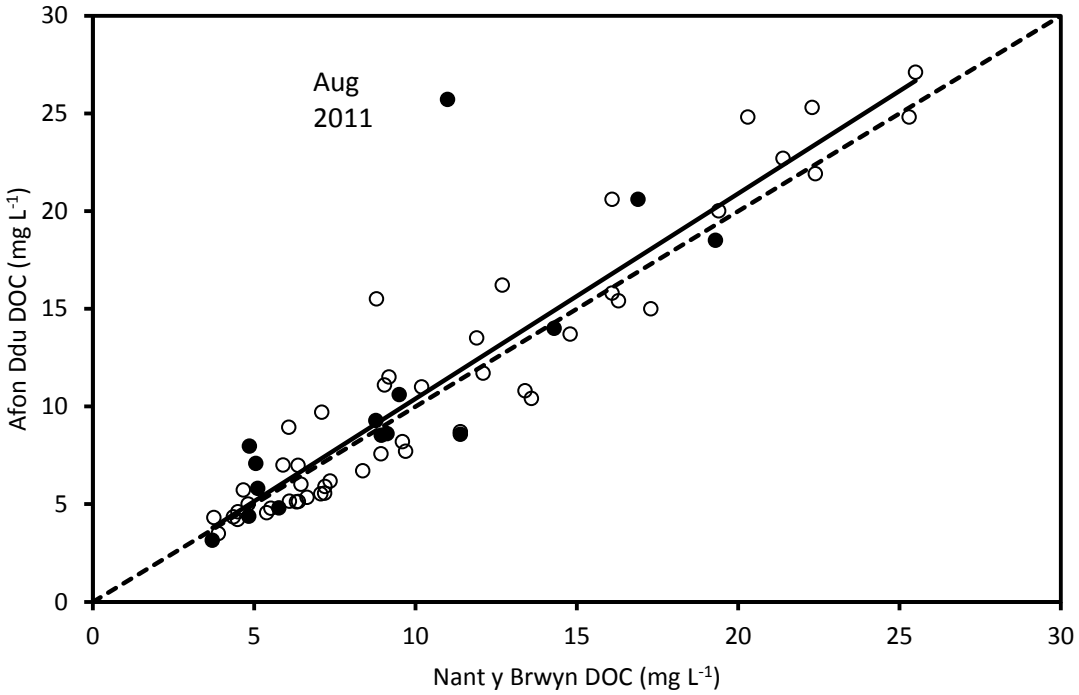


Figure 5. Regression of paired monthly stream samples for DOC concentration for the Afon Ddu and Nant y Brwyn catchments. Samples taken between January 2007 and April 2012. n = 63. r^2 = 0.84, or 0.91 if the August 2011 outlier is removed. Filled data points indicate samples taken after ditch blocking had occurred at the Afon Ddu. Dashed line indicates 1:1 relationship.

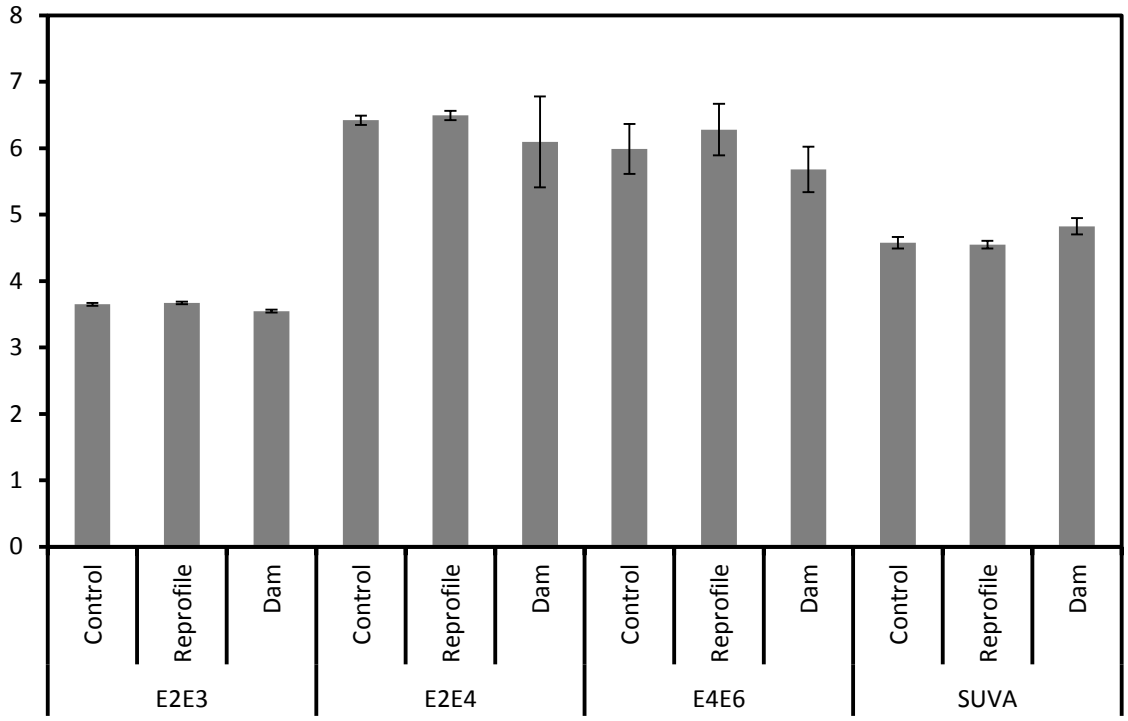


Figure 6. Mean values for ditch water for E2:E3 ratio, E2:E4 ratio, E4:E6 ratio and SUVA for each treatment. For each treatment n = 100 and is averaged from 25 monthly sampling trips from October 2010 to October 2012. Error bars show standard error of the mean. There is no significant difference between treatments.

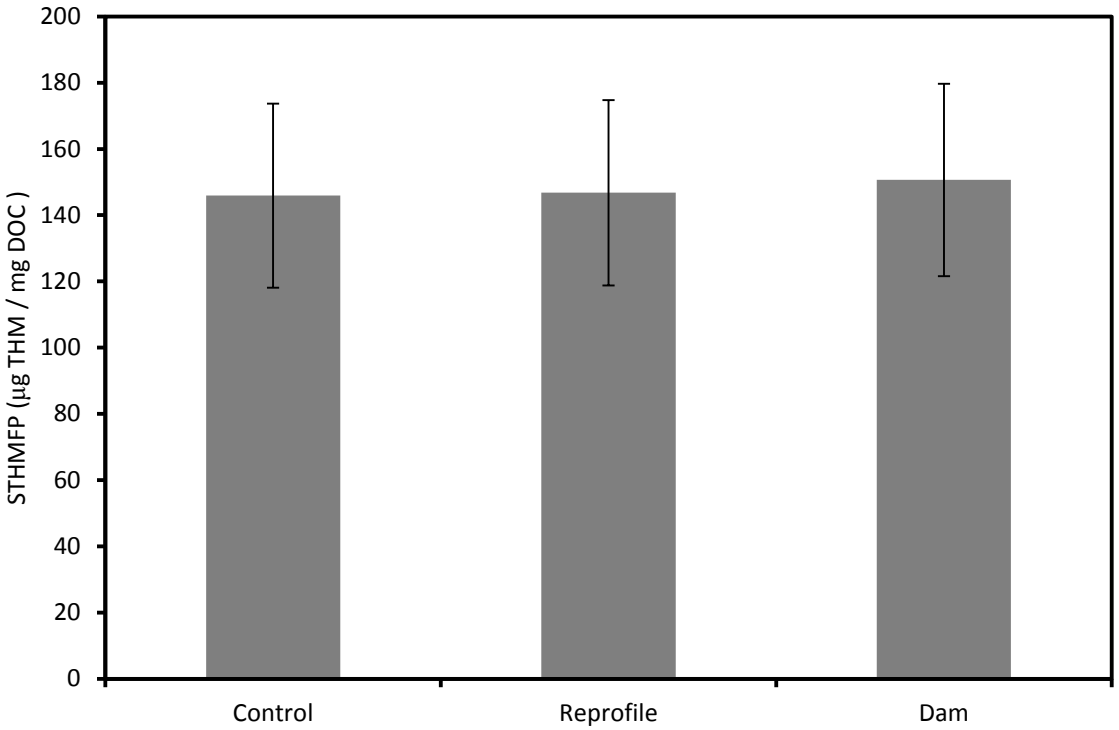


Figure 7. Standardised THMFP for ditch water samples taken in July 2012. *n* = 4 for each treatment. Error bars show standard error of the mean. There is no significant difference between treatments.

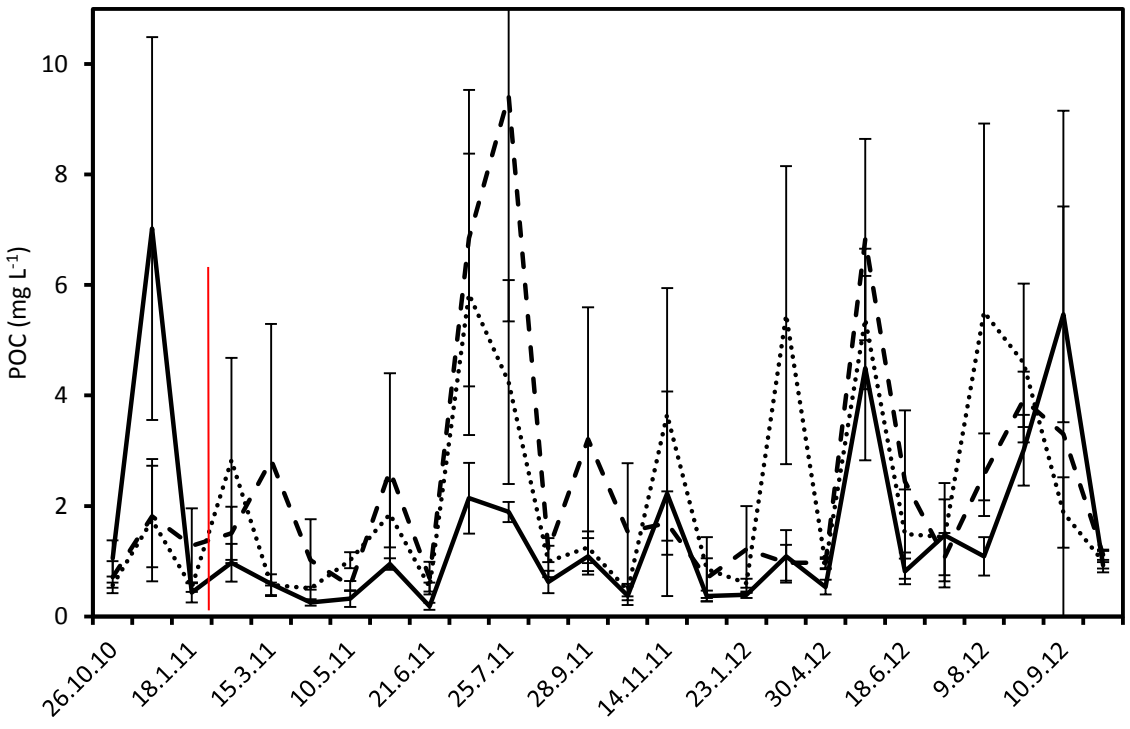


Figure 8. Monthly mean ditch water POC concentrations for open control ditches (continuous line), reprofiled ditches (dotted line) and dammed ditches (dashed line). *n* = 4 for each treatment, except for December 2010 and September 2012 (see appendix). Error bars show standard error of the mean. Red line indicates when ditch blocking occurred. There is no significant difference between treatments.

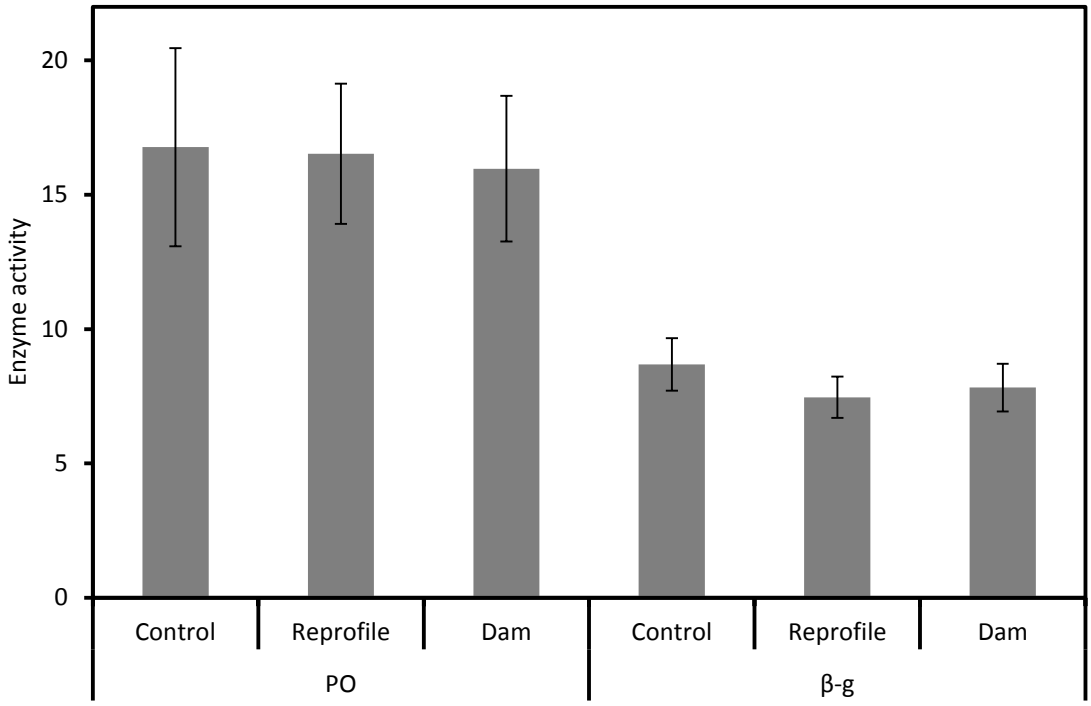


Figure 9. Mean enzyme activities for each treatment for phenol oxidase (PO, in n mol dicq g^{-1} min^{-1}) and β-glucosidase (β-g, in n moles g^{-1} min^{-1} MUF released). *n* = 20 for each treatment. Data are from five sampling trips between June and October 2011. Error bars show standard error of the mean. There is no significant difference between treatments.

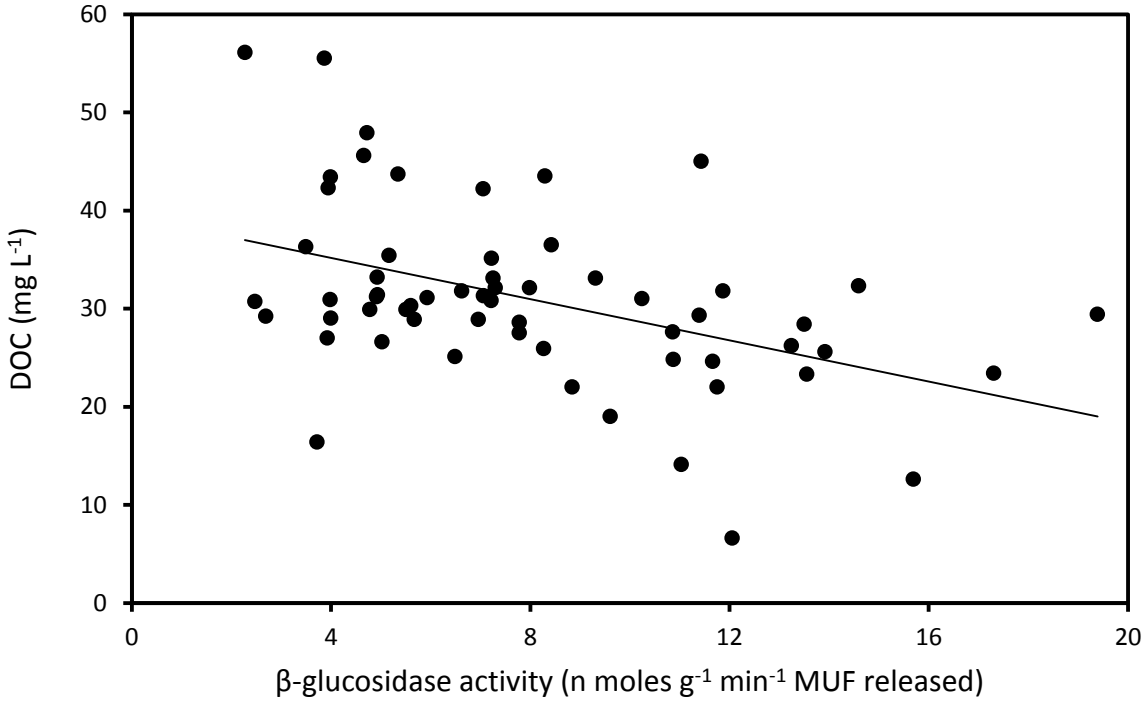


Figure 10. Relationship between β-glucosidase activity and DOC concentration in ditch waters. Data is from five sampling trips between June and October 2011. *n* = 60, r^2 = 0.20, p < 0.01.

5.3.3. Pore waters

Performing an ANOVA on the one set of pre-blocking pore water samples revealed no difference in DOC concentration or any of the spectrophotometric measures of DOC quality. Analysis of the post-blocking data revealed a significant difference in DOC concentrations, with mean post- rewetting values of 43.6 mg L^{-1}, 49.4 mg L^{-1}, and 47.6 mg L^{-1} for control, reprofiled and dammed ditches respectively (fig. 11). However, the differences between these mean values (range = 5.8 mg L^{-1}) are small when compared to the range between the treatment means for the one set of pre-blocking data (range = 15.6 mg L^{-1}). Highest DOC concentrations for each treatment occurred over consecutive sampling trips: 97.7 mg L^{-1} for dammed ditches in early July 2011, 73.8 mg L^{-1} for reprofiled ditches in late July 2011, and 63.5 mg L^{-1} for control ditches in August 2011. The July peak in blocked concentrations occurred just before the peak in stream DOC (fig. 4). Following this peak, concentrations for all three treatments show signs of convergence. Lowest concentrations were also recorded during different months for each treatment: 26.0 mg L^{-1} for control ditches in January 2011, 23.8 mg L^{-1} for reprofiled ditches in October 2012, and 22.9 mg L^{-1} for dammed ditches in January 2012. There was no significant difference in any of the four measures of DOC quality (fig. 12) following rewetting. Total means when all treatments were combined were: E2:E3 = 3.7, E2:E4 = 6.8, E4:E6 = 7.4, SUVA = 4.0.

ANOVA showed no significant difference in the activity of phenol oxidase or β-glucosidase (fig. 13) during summer and autumn 2011. Total means were 7.9 n mol dicq g^{-1} min^{-1} for phenol oxidase and 4.1 n moles g^{-1} min^{-1} MUF released for β-glucosidase. As for ditch waters, there was a significant inverse relationship between β-glucosidase activity and DOC (fig. 14) concentration, but no relationship between phenol oxidase activity and DOC.

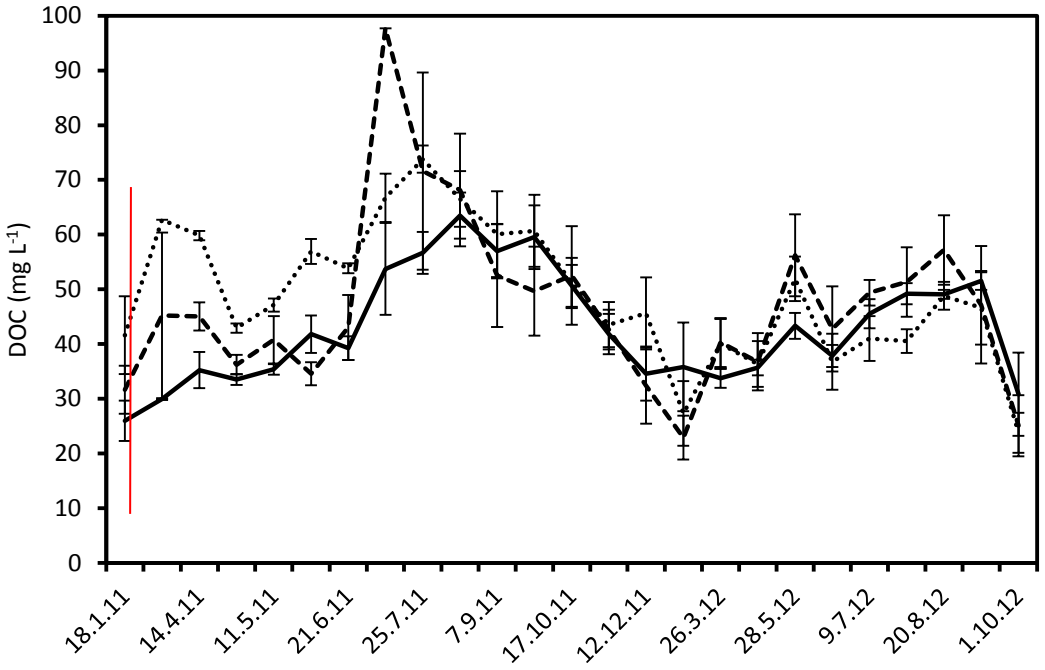


Figure 11. Monthly mean pore water DOC concentrations for open control ditches (continuous line), reprofiled ditches (dotted line) and dammed ditches (dashed line). *n* = 4 for each treatment for most months (see appendix for dates when this is not true). Error bars show standard error of the mean. Red line indicates when ditch blocking occurred. The difference in pre-blocking DOC is significant, but the post-blocking difference is not.

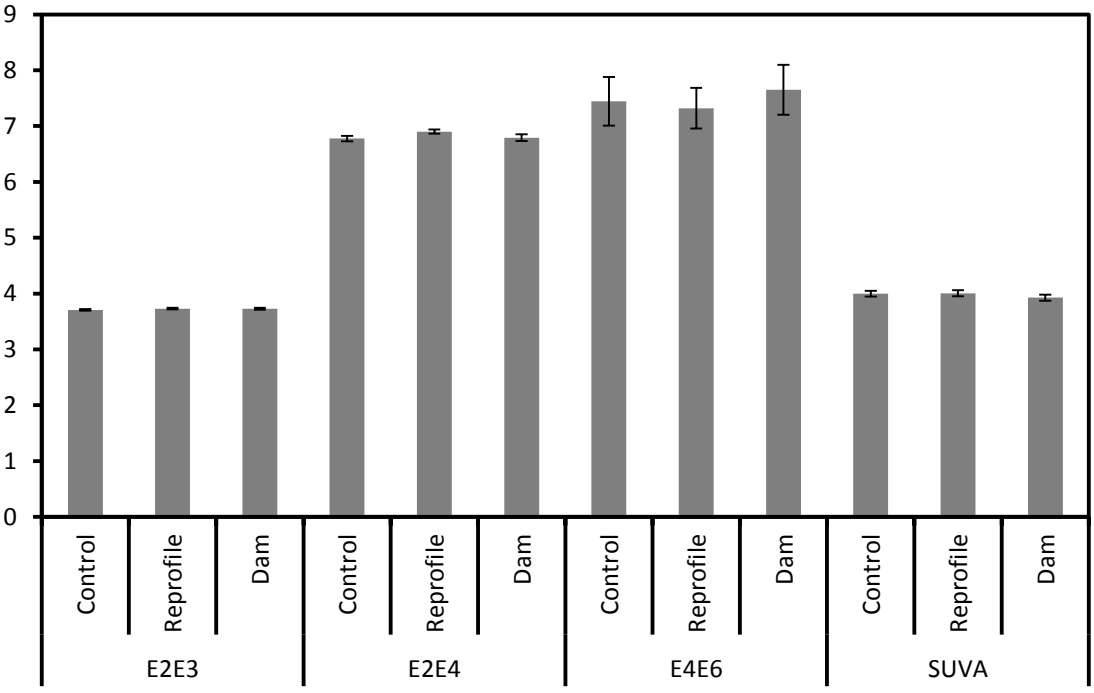


Figure 12. Mean values for pore water for E2:E3 ratio, E2:E4 ratio, E4:E6 ratio and SUVA for each treatment. For E ratios *n* = 86, 85 and 79 for control, reprofiled and dammed ditches respectively. For SUVA *n* = 85, 84 and 78 control, reprofiled and dammed ditches. Results are averaged from 23 monthly sampling trips from January 2011 to October 2012. Error bars show standard error of the mean. There is no significant difference between treatments.

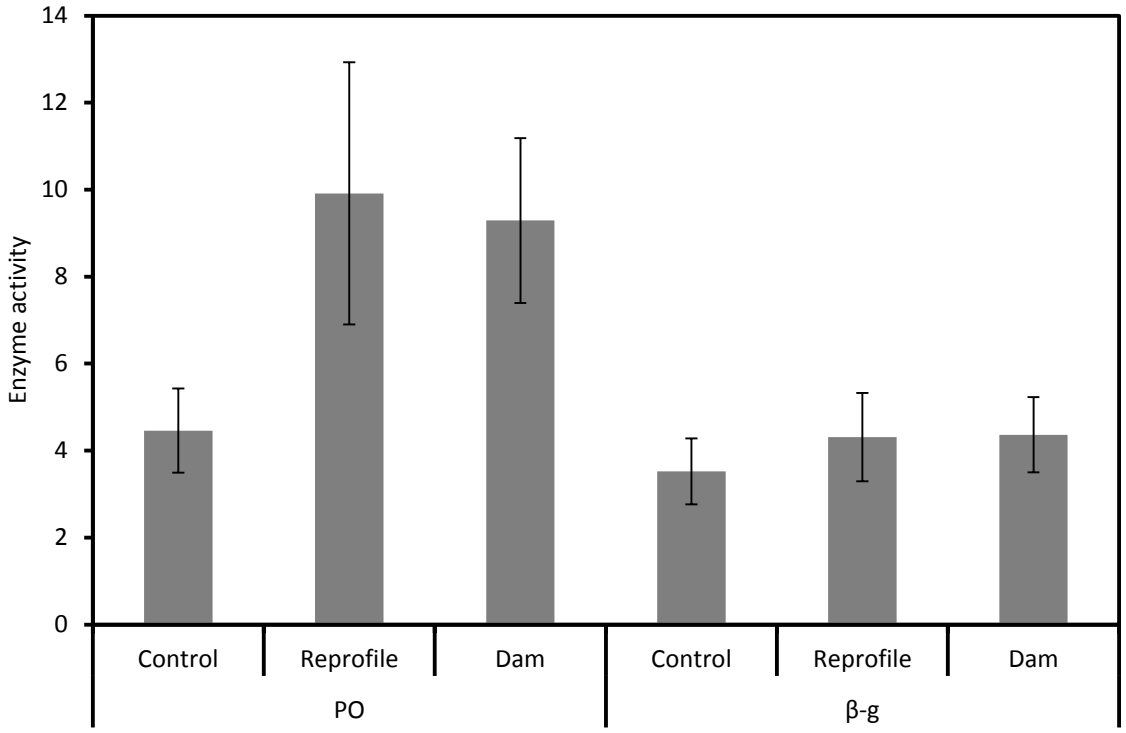


Figure 13. Mean enzyme activities for each treatment for phenol oxidase (PO, in n mol dicq g^{-1} min^{-1}) and β-glucosidase (β-g, in n moles g^{-1} min^{-1} MUF released). *n* = 12 for each treatment. Data is from three sampling trips between June and October 2011. Error bars show standard error of the mean. There is no significant difference between treatments.

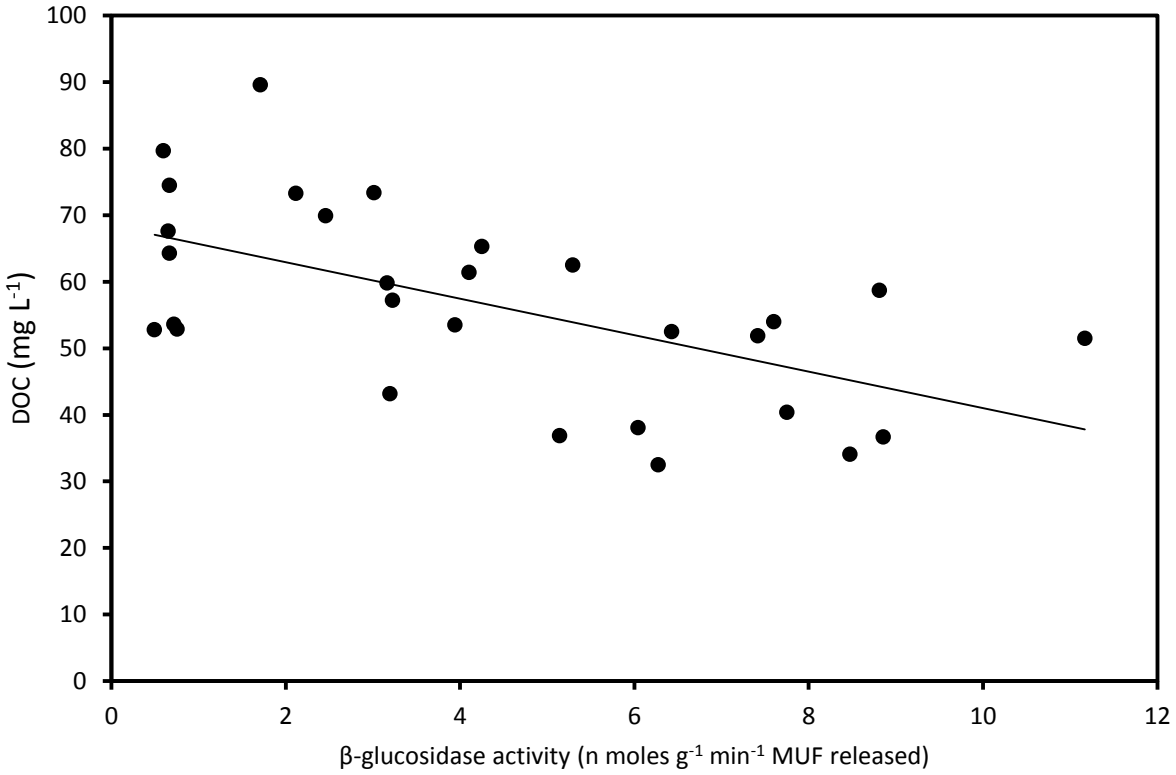


Figure 14. Relationship between β-glucosidase activity and DOC concentration in pore waters. Data is from three sampling trips between June and October 2011. *n* = 29, r^2 = 0.35, p < 0.01.

5.3.4. Overland flow

Although only post-blocking data was available for OLF samples, no significant difference in DOC concentration was found between treatments (fig. 15). Mean concentrations were similar to ditch water values: 21.3 mg L^{-1}, 24.1 mg L^{-1}, and 23.8 mg L^{-1} for the control, reprofiled and dammed ditches respectively. There could be a possible discrepancy here, as ditch waters were collected for two years whilst OLF samples were collected from summer 2011 to autumn 2012. This could potentially bias the mean concentration as data from two summers but only one winter is included. However, means from summer 2011 to summer 2012 revealed similar DOC concentrations: 21.6 mg L^{-1}, 25.0 mg L^{-1}, and 24.1 mg L^{-1} for control, reprofiled and dammed ditches. Lowest concentrations for all treatments occurred in October 2012, with a combined mean of 13.3 mg L^{-1}. Highest concentrations occurred in July 2011 for reprofiled and dammed treatments, with means of 37.8 mg L^{-1} and 43.4 mg L^{-1} respectively, and in August 2011 for control ditches, where a mean of 34.7 mg L^{-1} was recorded. There was no significant difference in any of the four measures of DOC quality (fig. 16). Total means when all treatments were combined were: E2:E3 = 3.8, E2:E4 = 6.6, E4:E6 = 5.7, SUVA = 3.6.

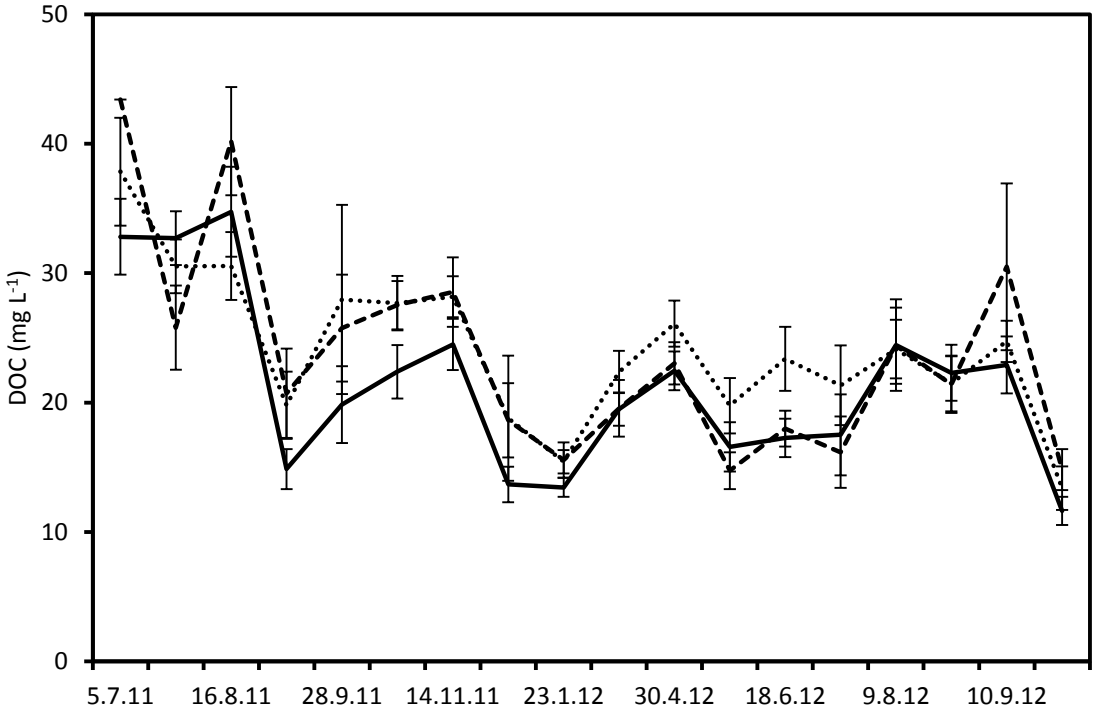


Figure 15. Monthly mean OLF DOC concentrations for open control ditches (continuous line), reprofiled ditches (dotted line) and dammed ditches (dashed line). *n* = 8 for each treatment (see appendix for dates when fewer samples were obtained). Error bars show standard error of the mean. There is no significant difference between treatments.

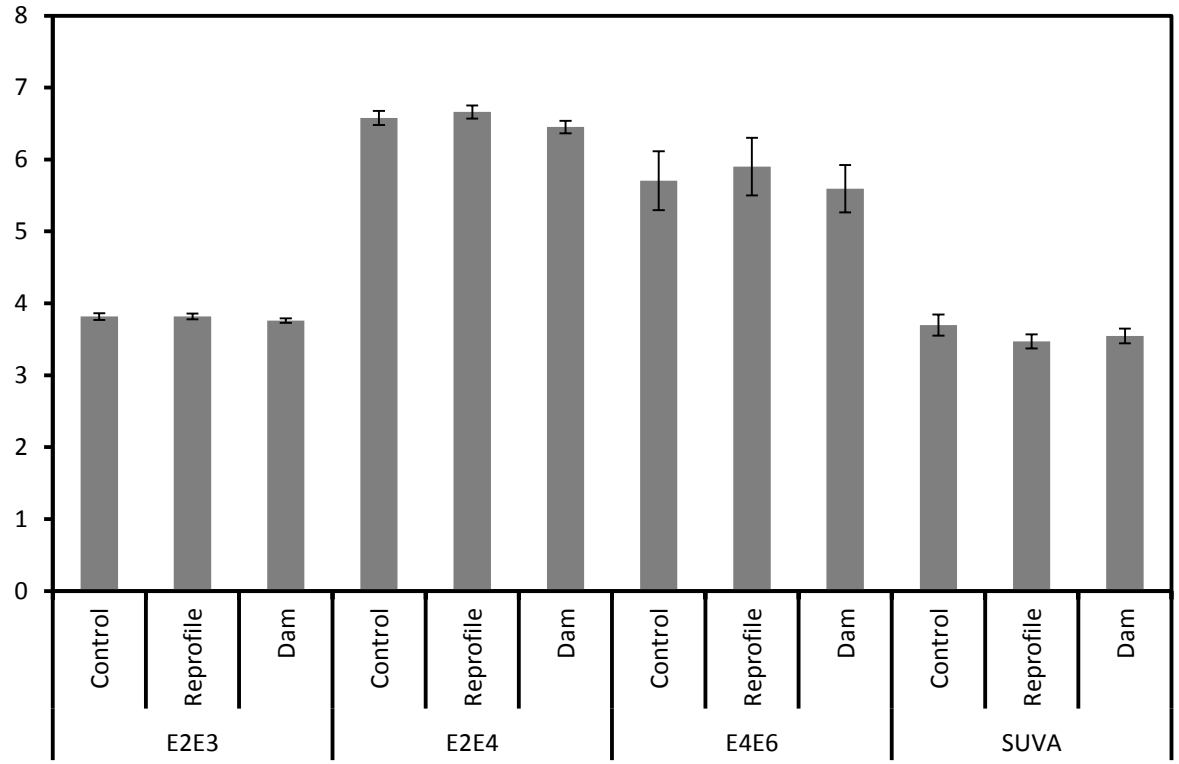


Figure 16. Mean values for OLF water samples for E2:E3 ratio, E2:E4 ratio, E4:E6 ratio and SUVA. Results are averaged from 8 sampling trips from January 2012 to October 2012. Error bars show standard error of the mean. There is no significant difference between treatments.

5.3.5. Relationships between sample types

Between 5.7.12 and 1.10.12 data were collected for all three sample types: ditch water, pore water, and OLF. Regression analysis of these data revealed significant, positive relationships between DOC concentrations for each sample type (fig. 17). The strength of this relationship was highest for OLF and pore water, and lower for ditch water and pore water, and ditch water and OLF. Comparing the monthly mean differences between the three sample types (figure 18) reveals that DOC concentrations are most similar between ditch and OLF samples. Differences between ditch and pore water, and pore water and OLF samples were much larger. On average, ditch water DOC concentration was 54% that of pore water, and OLF was 49% of pore water. Nevertheless, shared trends between data sets are visible, such as the peak in DOC concentration during May 2012 for ditch and pore water, and the shared drop in concentration for all three samples types in October 2012.

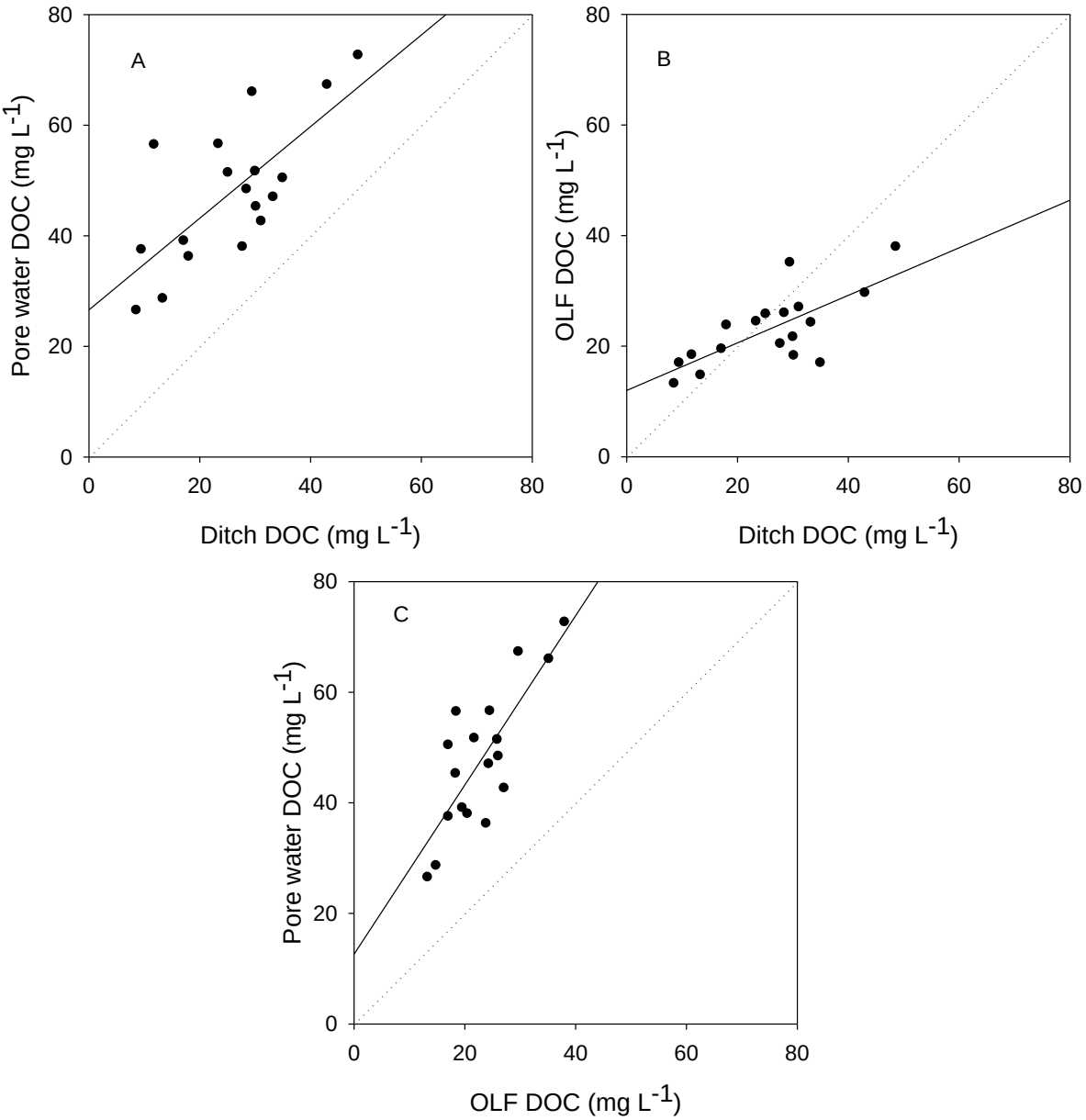


Figure 17. Relationships between DOC concentrations for each sample type. Data points are means of sample sets taken approximately monthly between 5.7.12 to 1.10.12. n = 18. r^2 values are: A = 0.52, B = 0.52, C = 0.63. Dashed lines show 1:1 relationship.

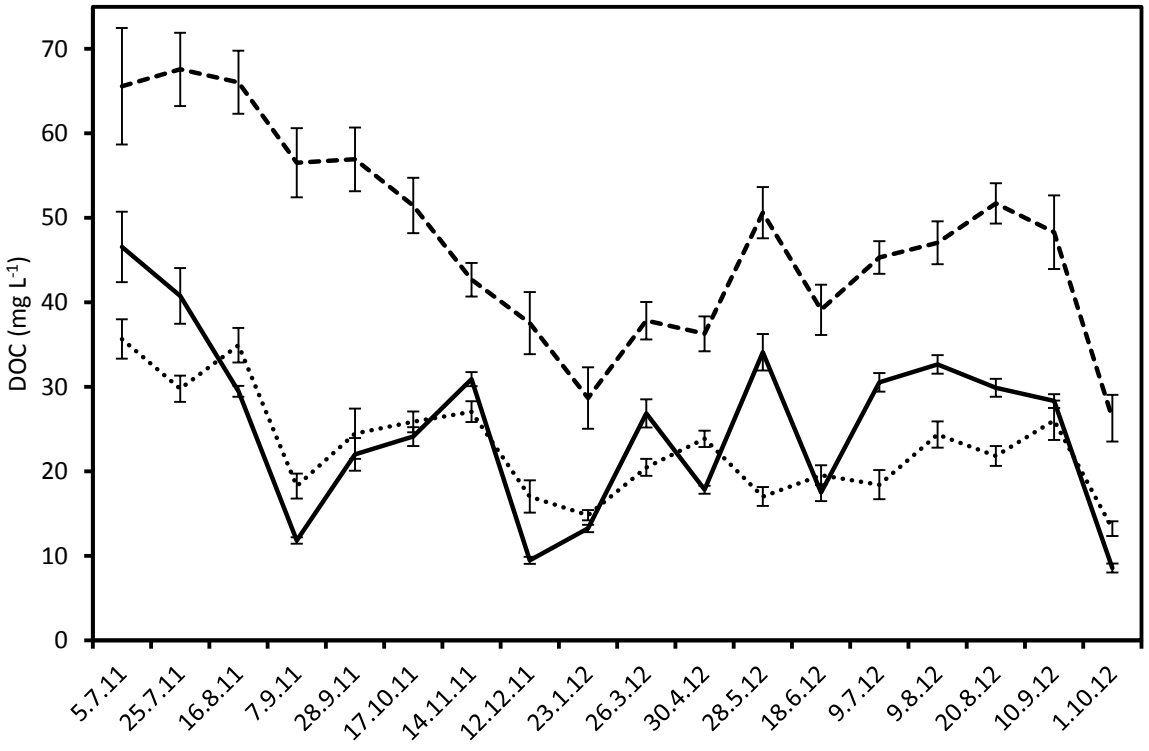


Figure 18. Total mean DOC concentration for each sample type: ditch water, pore water and OLF, for all sampling dates when all three sample types were collected. Generally n = 12 for ditch and pore water, and n = 24 for OLF. Solid line = ditch water, dashed line = pore water, dotted line = OLF.

5.4. Discussion

5.4.1. Ditch waters

There was no significant difference between open ditches and either of the two ditch blocking treatments for any of the measured determinands: pH, EC, sulphate concentration, DOC concentration, POC concentration, SUVA, E2:E3 ratio, E2:E4 ratio, E4:E6 ratio and THMFP. As with the results of Wilson *et al.*, (2011a) and Turner *et al.*, (2013), we demonstrate a decrease in DOC concentration with increasing scale; that is, concentrations were higher in ditches than in streams. DOC concentrations fluctuated throughout the study period, linked to seasonality and weather variations (Halliday *et al.*, 2012, Muller & Tankéré-Muller, 2012, Peacock *et al.*, 2013). The yearly data from the Afon Ddu stream that drains the experimental catchment clearly shows this seasonality, with a summer peak occurring each year. This is likely to be due to a lagged temperature effect (Clark *et al.*, 2005). For the stream data, it is clear that the seasonal cycle dominates over short-term episodic variability, and the results of Austnes *et al.* (2010) also show this for the Afon Ddu stream.

It is the stream dataset that gives the strongest hint of an effect of ditch blocking at the catchment (rather than ditch) scale. The summer peak in 2011, after ditch blocking took

place, showed a considerably higher DOC concentration at the experimental site relative to the Nant y Brwyn; an unblocked control catchment. Additionally, the high concentration was sustained for an extra month in the Afon Ddu. This is suggestive of either of two mechanisms; one possibility is that peatland disturbance raised DOC concentrations (Glatzel *et al.*, 2003), and the mechanical process of ditch blocking throughout a catchment, even when done sensitively, had a short-term effect on the ecosystem. In this case, during the reprofiling process borrow pits were dug to provide substrate for dams, vegetation was removed and replaced, and ditch bases were compressed to remove any hydrologically active peat pipes. Alternatively, there could be an enhanced flushing of DOC occurring as dams raise the water table. Even if a site-wide recovery of the water table has not occurred, an estimated 1600 dams have been created within the catchment. Each of these will raise the water table on a local scale and this is readily apparent as bog pools form behind dams. The cumulative effect of so many small-scale changes could lead to increased DOC flushing. Wallage *et al.,* (2006) proposed that after ditch blocking DOC was flushed from the peat at a depth of 10 cm, and the dams studied here may have raised the water table enough for this mechanism to function on a catchment scale. Additionally, POC concentrations in dammed ditches were extremely high during July and August 2011. As most of the ditches throughout the catchment were blocked using dams it is possible that concentrations in all ditches (not just those monitored for the experiment) were elevated at this time. This POC could have been converted to DOC as it moved through the catchment, with a resultant increase in DOC concentration in the Afon Ddu stream.

If this enhancement of DOC concentration at the experimental catchment is due to ditch blocking, and not some other effect, it only appears to be transient, and is not present at the ditch scale. After the flush is observed, concentrations in both streams return to parallel one another. As such, our results are comparable to other studies of ditch water chemistry following rewetting which also showed little or no effect on DOC concentrations immediately following ditch blocking (Wilson *et al.,* 2011a, Turner *et al.,* 2013), or even several years after blocking (Armstrong *et al.,* 2010, Ramchunder *et al.,* 2012). Given that changes in DOC flux without corresponding changes in concentration must be deemed highly unlikely to occur in these high-rainfall systems, we conclude that ditch blocking may not be a suitable technique to improve the quality of potable water draining from blanket bog catchments, at least within the first two years of blocking. On the other hand, if restoration projects proceed for other reasons, such as biodiversity enhancement (e.g. Mazerolle *et al.,* 2006) or greenhouse gas management (e.g. Komulainen *et al.,* 1999) then practitioners can be

secure in the knowledge that unwanted, adverse outcomes on water quality are unlikely, at least in the short to medium term. This conclusion is emphasised by the finding that there was no significant difference in THMFP between ditch treatments. Standardised THMFP was similar to values reported elsewhere from blanket peat (Gough *et al.*, 2012), but this study contains the first reported measurements of THMFP following ditch blocking.

What then, is the reason for a lack of response of ditch DOC concentrations to ditch blocking? One explanation could be that the original digging of the ditches had little effect, and therefore there was minimal effect for rewetting to reverse. In places the ditches had partly infilled naturally, and evidence suggests that abandoned ditches can lose their function through erosion (Fisher *et al.*, 1996, Holden *et al.*, 2007). The experimental ditches were relatively shallow, with a mean depth of 0.5 m, though it should be noted that further down hill in the blocked catchment ditches were frequently much deeper. Surveying on the Migneint by the National Trust has shown that vegetation besides unblocked ditches has changed from mire to heath communities, suggesting localised drying out since the ditches were dug. Nevertheless, blocking more heavily incised ditches might be more effective, but this needs to be tested.

Another reason for the absence of any major changes may be due to an associated lack of microbial response following rewetting. For example, Shannon & White (1994) demonstrated delayed recovery of methanogenic communities in ombrotrophic bogs following population declines caused by long-term exposure to lowered water levels. A study of a raised bog noted a lag time in the microbial response after restoration, and the authors hypothesised that ubiquitous microbial species that had dominated would continue to do so after restoration, with changes in the microbial community only occurring slowly (Francez *et al.*, 2000). It has been shown that the activities of extracellular enzymes that are involved in carbon cycling remain high after rewetting, as a legacy of previous aerobic conditions (Fenner & Freeman, 2011), and enzyme analysis of ditch samples from the Afon Ddu showed no significant difference between treatments for phenol oxidase or β-glucosidase activity. Changes to enzyme activities has been proposed previously as a mechanism that can alter DOC dynamics after ditch blocking (Wallage *et al.*, 2006) but no studies have been published to support this. It can therefore be hypothesised that no sustained changes in the microbial communities have yet occurred.

Another proposed hypothesis concerning rewetting and changes in DOC concentrations involves sulphate. Worrall *et al*. (2007a) suggested that ditch blocking could affect sulphate cycling. Aerobic conditions during drought events have been shown to

promote sulphide oxidation, leading to increased concentrations of sulphate and hydrogen ions, and thus a decrease in pH (Freeman *et al.*, 1994, Adamson *et al.*, 2001). In turn, this has been observed to decrease DOC concentrations (Clark *et al.*, 2005, Evans *et al.*, 2006, Clark *et al.*, 2006) due to changes in acidity and ionic strength (Evans *et al.*, 2012). As such, rewetting following ditch blocking could stimulate DOC mobility as sulphide oxidation decreases (Worrall *et al.*, 2007a, Daniels *et al.*, 2008). As ditch blocking did not lead to any significant changes in sulphate concentrations then this mechanism could not function.

POC concentrations were within the range of other reported values for the UK (Dawson *et al.*, 2002, Dawson *et al.*, 2004, Ramchunder *et al.*, 2012). Wilson *et al.* (2011a) noted no change in POC concentrations following ditch blocking, a conclusion that our statistics support. However, POC was extremely variable making statistical conclusions problematic, and POC concentrations were higher for both blocked treatments. There is a dearth of information on the effects of restoration and POC concentrations. It has been shown that drainage and ditch maintenance can lead to a sustained increase in sediment loading (Robinson & Blyth, 1982, Ahtiainen & Huttunen, 1999, Joensuu *et al.*, 1999, Nieminen *et al.*, 2010) and these POC losses increase with time due to the formation of soil pipes (Holden, 2006). Research also suggests that the erosion of ditch banks is important in supplying suspended sediment at a catchment scale, and that the sediment transport in drainage networks is supply limited (Marttila & Kløve, 2010). Ramchunder *et al.* (2012) found similar concentrations of POC in streams draining intact and ditch-blocked catchments, and these were considerably lower than concentrations in drained catchments. It could be that the blocked ditches are promoting sedimentation behind dams (Evans. M, *et al.*, 2006, Holden *et al.*, 2007) with a resultant decrease in POC export at the catchment scale, if not at the ditch scale.

5.4.2. Pore waters

As with ditch waters there was no significant difference in pH, EC or sulphate concentrations in pore water between treatments. DOC concentrations were close to those reported for similar sampler depths in other UK blanket bogs (Wallage *et al.*, 2006, Evans *et al.*, 2012). Compared to ditch waters, the dynamics and (lack of) response of DOC concentrations to ditch blocking were more complex. Whereas there were three sets of pre-blocking data available for ditch water samples, only one was available for pore waters. This set of pre-blocking data showed no significant difference between allocated treatments, suggesting that pore water DOC concentrations were uniform between treatments. Very little

can be inferred from a single pre-treatment sampling run, however. Post-blocking analysis then returned a significant difference between treatments, with mean DOC concentrations being slightly higher in both blocked treatments relative to controls. There is some evidence of a transient peak in DOC concentration for blocked ditches, occurring in July 2011, and coming one month before the DOC peak in the stream draining the catchment. As for the pulse of stream DOC, this could be explained as a disturbance or flushing effect. After this event, concentrations for all three treatments converge, suggesting that differences immediately following blocking may be real.

Despite this, only tentative conclusions on the effectiveness of ditch blocking can be drawn from this data. Firstly, despite the lack of significance in the pre-blocking data, the mean DOC concentrations covered a wide range of values: 26.0 mg L^{-1} for control ditches, 41.6 mg L^{-1} for reprofiled ditches, and 31.7 mg L^{-1} for dammed ditches. A lack of significance in this data set is likely to be due entirely to the small sample size. It seems probable that pore water DOC concentrations vary considerably across the site, in relation to spatial changes in hydrology and vegetation (Wickland *et al.,* 2007, Armstrong *et al.,* 2012, Sachse *et al.,* 2001), and that the relative contribution and effect of these changes can be modified by seasonality (Vestgarden *et al.,* 2010). Secondly, there was no significant treatment effect on DOC quality, as measured by SUVA, E2:E3 ratio, E2:E4 ratio, and E4:E6 ratio. Other studies have recorded changes in some of these measurements after ditch blocking and have cited them as indicators of a treatment effect (Wallage *et al.*, 2006, Worrall *et al.*, 2007a, Wilson *et al.*, 2011a). Thirdly, no difference in phenol oxidase or β-glucosidase activity was found between treatments, which might be expected to lead to a change in DOC concentrations (Freeman *et al.*, 2001a, Freeman *et al*., 2001b). Fourthly, no difference in sulphate concentration was found between treatments, which can influence DOC mobility (Evans. C, *et al.,* 2006, Clark *et al.,* 2006). The fact that DOC in pore waters was so variable over a small spatial scale calls into question the findings of Wallage *et al.* (2006), who concluded that ditch blocking reduced pore water DOC concentrations. Their study had no pre-blocking data, and sampling sites were geographically separated by up to 1 km. The effect of ditch blocking that they reported may actually have been due to natural differences between sampling sites. These findings highlight the urgent need for long term baseline data in restoration projects.

5.4.3. Overland flow

For OLF samples only post-blocking data were available, beginning five months after ditch blocking had occurred. There was no significant difference between treatments for pH, EC, sulphate concentration, DOC concentration or any of the four measures of DOC quality. Mean pH values were considerably higher than ditch or pore water and this indicates that OLF picks up alkaline material from the peat surface. This could be a slight artefact of the CSTs which will capture the first pulse of overland flow, which is when any soluble material on the peat surface will be picked up.

The lack of a treatment effect on DOC is expected considering the other results; a large proportion of OLF will be comprised of water that has been funnelled out of the blocked ditches by channels at dams. This hypothesis is supported by the similar DOC concentrations observed in ditch and OLF water. As there was no treatment effect on ditch DOC concentrations there was no associated difference in OLF.

To our knowledge this is only the second ditch blocking study to measure DOC concentrations in OLF, the first being that of Wallage *et al.* (2006). Despite using the same sample collection method as Wallage *et al.* (2006), DOC concentrations in OLF samples at the Afon Ddu catchment were higher, being approximately double those reported by Wallage *et al.* (2006) (21.3 - 24.1 mg L^{-1} compared to 8.5 - 12.6 mg L^{-1}). Sample collection from their study was from January to May, a shorter period than that reported here, but even if mean OLF DOC concentrations are calculated for the Afon Ddu for an identical period they are still higher. More generally there is a lack of reported data on DOC in OLF. Chapman (1993) recorded DOC concentrations between 11 - 32 mg L^{-1} in OLF in a peat catchment in mid Wales which is similar to this study. A study of tropical, mineral, acid soils recorded mean DOC in OLF as 19.7 mg L^{-1} (Johnson *et al.*, 2006). The authors noted substantial temporal variation in concentrations, a trait that has also been reported in organic soils (Hinton *et al.*, 1998).

Ditch blocking has been seen to increase OLF (Wilson *et al.*, 2011b), and OLF is an important runoff pathway in blanket bogs (Holden & Burt, 2003). Additionally Turner *et al.* (2013) showed that the rewetting-induced reduction in DOC export (as measured in drains and streams) decreased as spatial scale increased, suggesting an alternative flow pathway out of the blocked ditches. Considering these facts, it seems probable that DOC in OLF is the missing component of many ditch blocking studies. It is likely that ditch blocking simply funnels water around dams and out of ditches, creating OLF with DOC concentrations similar to ditch DOC. Eventually this DOC will re-enter drainage ditches or streams, and the time

span of this will depend on the gradient of the catchment, and whether ditches cut directly down the slope (as in this study), or at an angle across the gradient. Hinton *et al.* (1998) reached a similar conclusion concerning the importance of DOC in OLF in Canadian forested catchments, particularly at peak discharge. This interpretation therefore potentially calls into question the conclusions of other studies that suggest that ditch blocking successfully reduces DOC export purely by reducing water flux (Gibson *et al.*, 2009, Wilson *et al.*, 2011a), as unmeasured OLF will simply return DOC to the drainage system further downstream, potentially resulting in no net change in total DOC flux. To successfully determine the effects of ditch blocking on DOC concentrations, it may be necessary to monitor ditch water, pore water, and OLF within the restored area, as well as stream and river concentrations throughout the catchment.

5.4.4. Comparison of sample types

For ditch water, pore water, and OLF, there was very little difference in the E2:E3 ratio, with respective values of 3.6, 3.7, and 3.8. This indicates that the molecular weight and aromaticity of the DOC was similar for all sample types (Peuravuori & Pihlaja, 1997). SUVA displayed more differences between samples than the E2:E3 ratio, with values of 4.6, 4.0, and 3.6 for ditch water, pore water, and OLF respectively. Like the E2:E3 ratio, SUVA is a measure of aromaticity, with increasing values demonstrating increasing aromaticity (Weishaar *et al.*, 2003). The E2:E4 ratio, which has been cited as both a measure of humification (Park *et al.*, 1999), and as a comparison of the UV-absorbing functional groups to coloured ones in DOC (Selberg *et al.*, 2011, Graham *et al.*, 2012), was relatively similar across sample types. Values were 6.3, 6.8, and 6.6 for ditch water, pore water, and OLF. Differences in the E4:E6 ratio were larger, with values of 6.0, 7.5, and 5.7 ditch water, pore water, and OLF. Some researchers have proposed that the E4:E6 ratio is a measure of humification (Thurman, 1985, Summers *et al.*, 1987). Conventionally, this therefore suggests that pore water DOC is more fulvic acid-dominated than surface water, and similar differences between ditch and pore water have been noted previously (Wallage *et al.*, 2006, Wilson *et al.*, 2011a). However, it has also been argued that the E4:E6 ratio is unsuited to freshwater analysis (Peuravuori & Pihlaja, 1997, O'Driscoll *et al.*, 2006), with conflicting E2:E4 and E4:E6 ratios being reported (Park *et al.*, 1999). Wilson *et al.* (2011a) concluded that an increase in the E4:E6 ratio since ditch blocking was representative of a decrease in DOC aromaticity, colour, and decomposition, and therefore an increase in lability. However, analysis of time series data from the Afon Ddu study site showed that the E4:E6 ratio was

subject to large fluctuations between months in both ditch and pore water, and that the other three measures of DOC quality were more stable and therefore more appropriate to characterise DOC (refer to section 3.3.3). These data and publications clearly show that drawing conclusions from the use of only one measure of DOC quality may be unreliable.

All three sample types displayed significant, positive relationships between DOC concentrations; that is, when DOC concentrations were high in ditch water, they were also high in pore water and OLF. This is markedly evident in October 2012, where lowest DOC concentrations were observed for ditch water, OLF, and pore water for the reprofiled treatment. This is most probably due to biogeochemical mechanisms that are initiated by seasonality and weather events (Halliday *et al.,* 2012, Muller & Tankéré-Muller, 2012, Peacock *et al.,* 2013), and show how these factors affect both pore water and surface water simultaneously. Although no relationship was found between DOC concentration and phenol oxidase activity, a significant inverse correlation was found between DOC and β-glucosidase activity in soil samples associated with ditch water and pore water. Freeman *et al.* (1997) found the same relationship for soil samples from a peatland in mid Wales, and concluded that DOC represented a substrate for β-glucosidase, with the metabolic products then being microbially degraded under anaerobic conditions. It may be that spatial variation in β-glucosidase activity is controlled by localised changes in pH, water table, moisture, and vegetation (Williams *et al.,* 2000, Fenner *et al.,* 2005, Straková *et al*, 2011). As such, the activity of this extracellular enzyme could be responsible for the variable concentrations of pore water DOC.

As a final note, these processes control DOC production in pore water, and approximately 50% of this is leached to surface water. The similar timing and concentrations of ditch water and OLF imply that they are essentially the same thing, but travelling via different routes. This calls into question the validity of DOC flux studies that only measure ditch water. To reach robust conclusions, a full catchment-scale before-after-control-impact (BACI) approach may be necessary, with accurately defined catchments allowing total runoff to be captured.

5.4.5. Conclusions

Our results show that ditch blocking has had no significant effect on DOC concentrations in the short term, in the first twenty months after blocking. Additionally, there has been no effect on pH, EC, or DOC quality as ascertained using four different spectrophotometric measurements. This is true for ditch water, pore water, and OLF water.

No clear change was detected in POC concentrations, although mean concentrations were higher in blocked ditches. A limited analysis of ditch water samples for THMFP showed that ditch blocking did not lead to a change in the formation of disinfectant by-products following water treatment by chlorination. Possible reasons for the absence of a treatment effect include the facts that rewetting had no effect on sulphate concentrations or extracellular enzymes activities, both of which affect DOC dynamics. There was the suggestion of a peak in pore water DOC in blocked ditches during the summer following rewetting, which was then followed by enhanced DOC concentrations in the stream draining the catchment. This may have been due to ecosystem disturbance during blocking or a flush of DOC out of the system. However, this effect was transient, and given the limited number of samples somewhat uncertain.

This is only the second ditch blocking study to measure DOC in OLF, and the first study to measure DOC for pore water, ditch water and OLF in combination. DOC in OLF was of similar concentrations to that in ditches, and we conclude that ditch blocking, rather than reducing water (and hence DOC) fluxes, may simply have redirected water out of ditches onto the peat surface, where it travels downslope to rejoin the drainage network with a more or less unchanged DOC concentration. As such, those studies that postulate that ditch blocking is an effective way to manage DOC by lowering water fluxes down ditches may have missed an important pathway for water and DOC loss from ditch-blocked hillslopes. Clearly there is an urgent need for studies that consider both the flux of OLF and DOC concentrations, to establish estimates of DOC flux transported as OLF.

To conclude, our data do not provide clear evidence that ditch blocking is an effective method to reduce DOC concentrations in blanket bog drainage waters, at least in the short term. Further measurements and additional studies (including pre-restoration data and preferably incorporating all flow pathways and/or undertaken at the larger catchment scale) are required in order to assess whether these results are general, and whether clearer benefits might be obtained over longer periods. More positively, our data do demonstrate that peatland rewetting (undertaken for other reasons such as biodiversity or carbon sequestration) is unlikely to cause deleterious short-term peaks of DOC in water supplies. This study highlights the importance of measuring DOC in surface and pore water, as well as prescribing caution to the use of limited measurement techniques of DOC quality, as different spectrophotometric proxies can have conflicting results. Additionally, we stress that to fully understand ecosystem responses to rewetting, variables such as extracellular enzyme activity and sulphate concentration should be measured to fully disentangle the peatland

biogeochemistry. Finally, there is a lack of data concerning DOC concentrations in OLF, and this is not just limited to peatlands. We therefore echo the call of Hinton *et al.,* (1998) that more research on this subject is needed.

Appendix

Table 1. Ditch 4 data is removed from the pH mean as it showed anomalous biogeochemistry, indicative of a groundwater emergent point, with a higher pH.

Figure 1. For first ten sampling occasions (26.10.10 – 5.7.11) *n* = 3 for dammed ditches. The original sampling location showed anomalous biogeochemistry, indicative of a groundwater emergent point. As such, a new sampling location was established several metres up-ditch.

Figure 6. Months when *n* does not equal 4 for each treatment. C = control ditches, R = reprofiled ditches, D = dammed ditches. 16.12.10 *n* = 3 for C and D. 10.9.12 *n* = 2 for D.

Figure 7. Months when *n* does not equal 4 for each treatment. C = control ditches, R = reprofiled ditches, D = dammed ditches. 15.3.11 *n* = 2 for C and D, and *n* = 1 for R. 14.4.11 *n* = 3 for D and R. 11.5.11 *n* = 3 for C, R and D. 7.6.11 *n* = 2 for D. 5.7.11 *n* = 3 for C and R and *n* = 1 for D. 25.7.11 *n* = 3 for C and *n* = 2 for D. 28.9.11 *n* = 3 for D and R. 26.3.12 *n* = 3 for D. 28.5.12 *n* = 3 for C and D. 10.9.12 *n* = 3 for C and R. 1.10.12 *n* = 3 for C and D.

Figure 13. Months when *n* does not equal 8 for each treatment. C = control ditches, R = reprofiled ditches, D = dammed ditches. 5.7.11 *n* = 5 for C, *n* = 1 for D, *n* = 3 for R. 25.7.11 *n* = 7 for C, *n* = 6 for D, *n* = 5 for R. 16.8.11 *n* = 7 for D. 7.9.11 *n* = 6 for D. 28.9.11 *n* = 7 for D. 9.7.12 *n* = 7 for D. 20.8.12 *n* = 7 for C. 1.10.12 *n* = 7 for C.

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Natural revegetation of bog pools after peatland restoration involving ditch blocking – the influence of pool depth and implications for carbon cycling

6.1. Introduction

Northern peatlands are a vitally important component of the global carbon cycle, storing an estimated stock of 547 Pg of carbon (Yu *et al.*, 2010). Additionally, peatlands are important for biodiversity, as numerous species of invertebrates, birds and bryophytes are restricted to such habitats (Warner & Asada, 2006). On both local and global scales, peatlands have been damaged through drainage and peat extraction, but attempts are now being made to restore them through ecological engineering techniques.

In the United Kingdom (UK) peatland restoration is typically carried out through the blocking of drainage ditches (i.e. rewetting) with the aim of raising the water table and encouraging the establishment of peat-forming plant species such as *Sphagnum*. Blocking takes place using dams constructed from a variety of materials including peat, plywood, plastic and heather bales (Armstrong *et al.*, 2009). A more complex method is that of reprofiling, where dams are constructed and the base of the ditch is compressed by mechanical force to destroy any soil pipes that might flow beneath the ditch. Following rewetting pools form behind dams, and in natural peatlands these pools are critical biodiversity hotspots (Mazerolle *et al.*, 2006).

There are few studies of pools and of the effect of ditch blocking on peatlands that have solely been drained, as most of the literature has focussed on cutaway peatlands where drainage and harvesting have both occurred. In an Irish study on an abandoned cutaway peatland, pools of standing water were colonised by *Juncus bulbosus* var. *Fluitans* which spread to provide a substrate for the growth of *Sphagnum cuspidatum* and *Sphagnum auriculatum*. The stabilisation of the water table using a peat bund increased the rate of this re-colonisation, resulting in the spread of these same pool species after two years (Farrell & Doyle, 2003). It has been noted elsewhere that *S. cuspidatum* can act as an aquatic pioneer species by forming a semi-floating raft suitable for further colonisation by other species (Money & Wheeler, 1999). For the restoration of pools in a Canadian cutaway peatland, *Sphagnum* species were taken from a natural site and transferred using the 'moss layer transfer technique'. After three growing seasons *Sphagnum* cover reached 50% along pool margins (Poulin *et al.*, 2011). Another Canadian study found that the stocking of pools with aquatic plants had no effect on vegetation colonisation, and that four years after restoration

pH and dominant plant species differed from natural pools. The authors suggested that an increased stocking density might promote vegetation recolonisation (Mazerolle *et al.*, 2006).

Another pioneer plant of peatlands is *Eriophorum vaginatum*. Ditch blocking has been observed to promote the spread of *E. vaginatum* (Komulainen *et al.*, 1998, Lavoie *et al.*, 2005), and it can colonise pool margins (Poulin *et al.*, 2011). It typically colonises bare peat with a lower water table, but can tolerate higher water tables (Kivimäki *et al.*, 2008). The vegetation response to the creation of pools is important from the perspective of the carbon and greenhouse gas budget of a site. Some vascular plants can act as 'chimneys' by transporting gas directly to the atmosphere via their aerenchymatous tissue, and they also provide substrates for methanogenesis via root exudation and litter production (Marinier *et al.*, 2004).

As vegetation communities change following peatland restoration, it is possible that an associated change occurs in the fluvial carbon balance. Dissolved organic carbon (DOC) is exported from peatland catchments in drainage waters, and its production is affected by numerous factors, including vegetation (Palmer *et al.*, 2001). For example, Armstrong *et al.* (2012) noted that *Calluna* was associated with high DOC concentrations in both a plot-scale (pore water) and a ditch-scale (surface water). DOC is of interest for various reasons: it is a component of the carbon cycle; it can affect the functioning of aquatic ecosystems (Karlsson *et al.*, 2009); it is expensive to treat in raw water supplies, and it can have negative effects on human health due to trihalomethane formation during water treatment (Chow *et al.*, 2003).

In this study, we investigated the recolonisation of bog pools that were formed through ditch blocking. We hypothesised that shallow pools would be dominated by *E. vaginatum* whilst *Sphagnum* species would form as floating rafts as pool depth increased. Additionally, a link between pool vegetation and characteristics, and DOC was investigated. Finally, the dams are specially designed to feature small overflow paths that channel water either side of the dam. By measuring DOC concentrations in transects of successive downstream pools we also aimed to resolve whether DOC was produced or degraded between pools, leading to changes in concentrations down pool sequences.

6.2. Materials and Methods

The study was carried out at the head of the Afon Ddu catchment (latitude 52.97°N, longitude 3.84°W) on the Migneint, an Atlantic blanket bog, in Snowdonia National Park, north Wales (UK). The bog has been extensively drained, with ditches spaced 10-20 m apart, but no peat harvesting has occurred. Ditches were blocked in February 2011 using the

reprofiling method and peat dams, and pools of various sizes formed behind. Pools are typically 2 m wide and 2-3 m long, but much larger ones have formed. Approximately 1600 pools have been created. Sampling took place in August 2012. A random selection of 60 pools was made. This included three transects where either five or seven successive pools in the same ditch were surveyed down-slope. The dimensions of each pool were measured, and a depth measurement taken from the centre of the pool. Vegetation cover at the surface of the pool was estimated by sight to the nearest 5% (except for very low incidences of cover that were estimated at 2.5%), and the plant species recorded. A water sample was taken from the middle of each pool for lab analysis and stored in the dark at 4^{o}C. All pools were surveyed on the same day to allow a robust comparison, as DOC concentrations can fluctuate seasonally, and according to the prevailing meteorological and hydrological conditions. Additionally, pool size may change following drought or precipitation. Seven control water samples were taken from an unblocked ditch to compare against pool samples.

Water samples were analysed the day after collection. Absorbance was measured at a wavelength of 263 nm using a Molecular Devices M2e Spectramax plate-reader. DOC concentrations were then calculated from this absorbance using a previously established calibration curve for the site. This wavelength was chosen as it gave the highest r^2 (0.91) value and lowest residual variance (RMS = 16.9).

A linear regression model was used to investigate the relationship between pool characteristics and vegetation cover. A multiple regression model using pool depth, area, and species vegetation cover as predictors of DOC was not significant, so a simpler method was used. Mean values were calculated for pools with ≥ 50% cover of *Sphagnum* or *Eriophorum* (one pool where both vegetation types were present at 50% cover was not included). The area from each pool to the top of the slope was measured and used as an estimate of upstream contributing area, and therefore flow rate, although the contributing area was somewhat uncertain due to changes to drainage patterns induced by the restoration work. Statistical analysis was performed using SPSS v16.0.1 (IBM Corporation, http://www-01.ibm.com/software/analytics/spss/products/statistics/).

6.3. Results

6.3.1. Physical pool characteristics and vegetation colonisation

There was considerable variation in the physical characteristics of the pools and the proportion of vegetation colonisation (table 1). Pools were mainly colonised by *E. vaginatum* (with some *Eriophorum angustifolium*) and *Sphagnum* species (predominantly *S.*

cuspidatum); respective means were 37% (standard error = 3.2%) for *Sphagnum* and 38% (SE = 3.6%) for *Eriophorum*. Two pools showed significant amounts of algal growth, and a small area of one pool had been colonised by *Juncus effusus*. Both mean and median vegetation cover values were above 75%, and only seven pools had less than 50% vegetation cover, indicating a high level of recolonisation with only small areas of open water.

Table 1. Summary statistics for data from 60 pools. SE is the standard error of the mean.

	Mean	SE	Median	Minimum	Maximum
Depth (m)	0.41	0.04	0.33	0.03	1.15
Width (m)	1.96	0.09	1.9	0.7	4.2
Length (m)	2.78	0.36	1.8	0.7	17.9
Area (m^2)	6.37	1.04	3.48	0.63	46.54
Vegetation cover (%)	76	3.03	81	10	100
DOC (mg L^{-1})	22.09	0.42	21.6	16.75	30.29

There was a strong negative relationship between pool depth and *Eriophorum* colonisation (figure 1), and at depths greater than 0.5 m *Eriophorum* only grew on the shallow pool margins. The relationship between pool depth and *Sphagnum* cover was positive but weak (figure 2), with large variations in cover at deeper depths; for example, at approximately 0.8 m depth different pools displayed *Sphagnum* cover from 0% to 90%. There was no evidence that upstream contributing area (and therefore flow rate) influenced species cover.

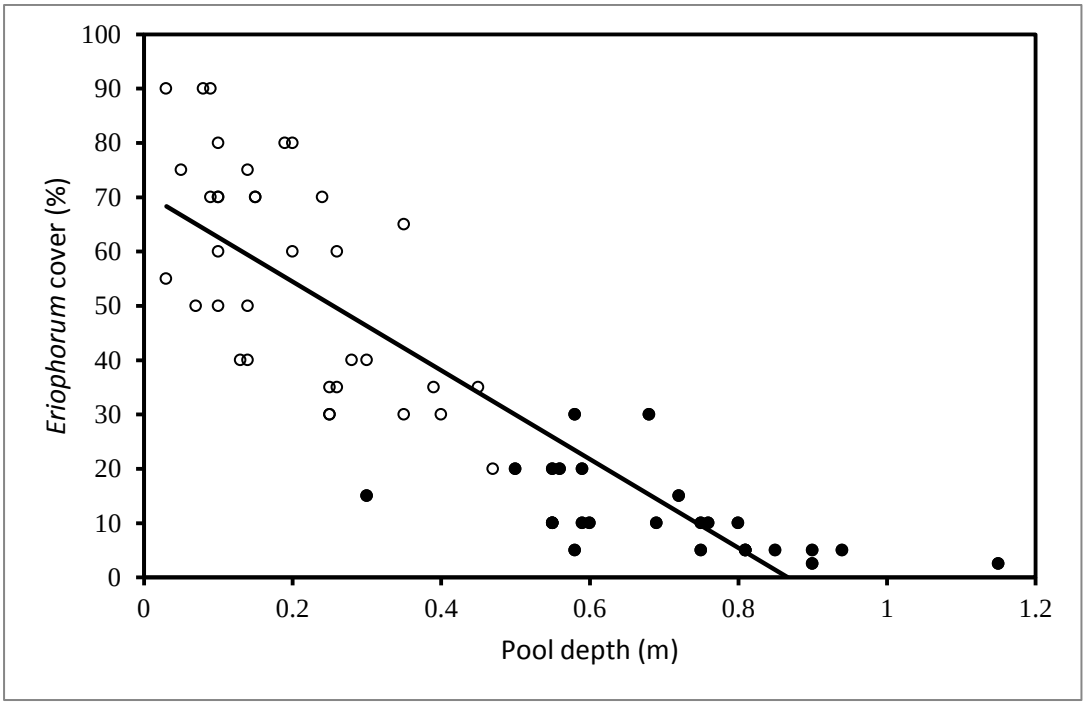

Figure 1. Percentage cover of *Eriophorum* versus pool depth for 60 pools. Linear regression $r^2 = 0.74$, $p < 0.001$. Filled circles indicate pools where *Eriophorum* was only present in the shallow pool margins.

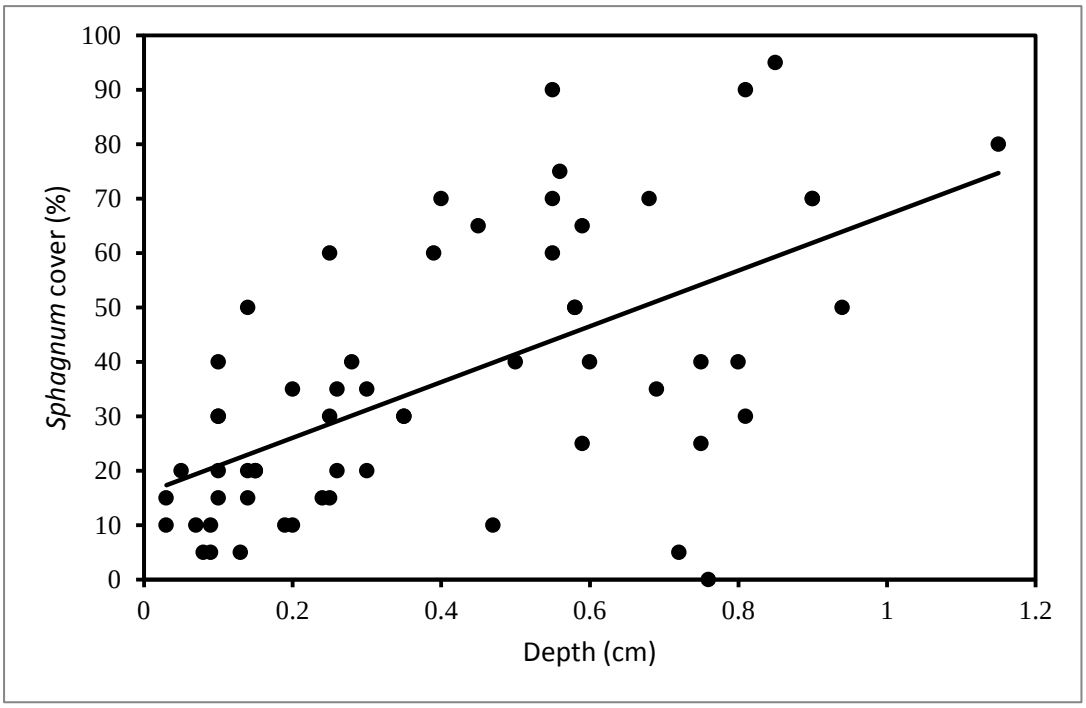

Figure 2. Percentage cover of *Sphagnum* versus pool depth for 60 pools. Linear regression $r^2 = 0.35$, $p < 0.001$.

6.3.2. DOC concentrations

Mean pool DOC concentration was 22.09 mg L^{-1} (SE = 0.42 mg L^{-1})(table 1). DOC concentration was 22.8 mg L^{-1} (n = 18, SE = 0.8 mg L^{-1}) for *Sphagnum* pools, and 21.6 mg L^{-1} (n = 21, SE = 0.6 mg L^{-1}) for *Eriophorum* pools. This difference was not significant at p = 0.05 (two-sample t-test). Further analysis revealed no significant relationships between DOC concentrations and pool area or depth. The results from the three ditch transects measuring DOC concentrations in each successive down-slope pool showed that there was no consistent cumulative production or degradation of DOC down the transects (figure 3). The mean DOC concentration for samples from the unblocked ditch was 20.5 mg L^{-1} (n = 6, SE = 0.4 mg L^{-1}); one sample was removed as its concentration was very low (9.76 mg L^{-1}), possibly due to the ditch intersecting with a groundwater emergence point.

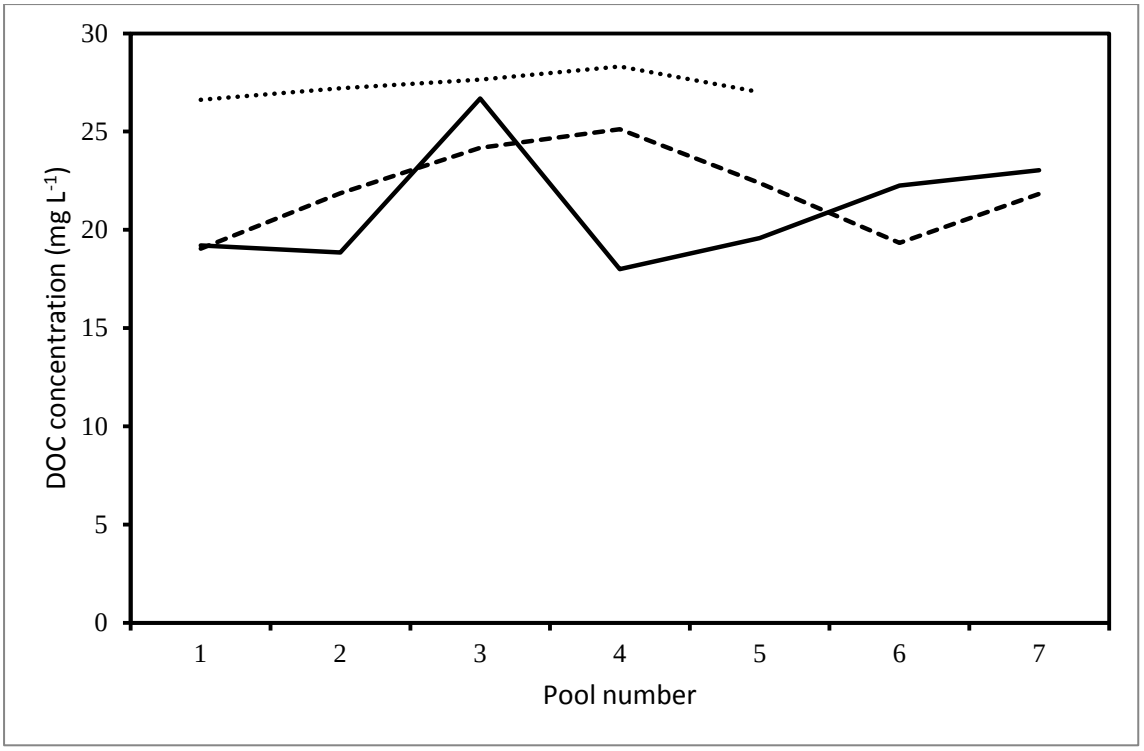

Figure 3. DOC concentrations for three ditch transects (indicated by different lines), where successive down-slope pools were surveyed. Pool number 1 is at the top of the transect, and each subsequent pool is the next one down-slope along the ditch.

6.4. Discussion

6.4.1. Vegetation colonisation

Our results show that ditch blocking has been successful in creating bog pools with consistently high rates of vegetation colonisation after eighteen months. *E. vaginatum* and *S. cuspidatum* were the primary colonising species, with additional colonisation by *E. angustifolium*, *Juncus effusus*, algae, and other *Sphagnum* species. Our hypothesis that shallower pools would favour *Eriophorum* growth was supported, with *Eriophorum* cover decreasing linearly with pool depth. At depths greater than 0.5 m *Eriophorum* was restricted to shallow pool margins, and cover was reduced to ≤5% at depths greater than 0.8 m. Poulin *et al.* (2011) noted a similar response, with pool margins being colonised by *Eriophorum*, and suggested that this invasion might be a transient phase in the early stages of restoration. *Sphagnum* cover increased with pool depth, although this relationship was weaker than that between *Eriophorum* and depth, with large variation in cover at greater depths. There are several possible reasons for this. It has been suggested that deep pools that form behind dams can make vegetation establishment difficult, as the low level of light penetration reduces the rate of vegetation colonisation (Ramchunder *et al*, 2009). DOC can affect photic depth

(Monteith *et al.*, 2007) but this seems an unlikely control on vegetation colonisation as *Sphagnum* cover and DOC concentration were unrelated. Additionally, DOC effects on photic depth would only impede vegetation growth if *Sphagnum* was establishing from the base of the pool, not as floating mats. Boatman (1977) established that differences in nutrient supply could explain *S. cuspidatum* growth in bog pools, and there is some spatial variation in ditch nitrate concentrations at the experimental site (M. Peacock, unpublished data). Another possible explanatory factor could be the profile of the ditch sides, as steep sides could impede the establishment of *Sphagnum*.

Numerous restoration studies have reported high methane fluxes from areas of *Eriophorum* (Mahmood & Strack, 2011, Tuittila *et al.*, 2008, Marinier *et al.*, 2004, Komulainen *et al.*, 1998), but its colonisation on bare peat does lead to the creation of a carbon dioxide sink (Tuittila *et al.*, 1999). Balanced against this, *S. cuspidatum* has been shown to consume methane through symbiosis with methanotrophs (Raghoebarsing *et al.*, 2005) and this mechanism is found in *S. cuspidatum* globally (Kip *et al.*, 2010). *Sphagnum* is also desirable as it enhances the carbon sink of the ecosystem and, for Boreal peatlands, increases the strength of this sink in spring and autumn, relative to vascular plants (Kivimäki *et al.*, 2008). Contrary to this, some studies have not recorded high CH_4 fluxes from *Eriophorum* (e.g. Roura-Carol & Freeman, 1999, Dinsmore *et al.*, 2009, Wilson *et al.*, 2013) and it has been hypothesised that aerenchymous tissue also facilitates oxygen ingress into the rhizosphere, thus leading to decreased methanogenesis. Furthermore, *Sphagnum* has sometimes been observed to emit large fluxes of CH_4 (Wilson *et al.*, 2013). Clearly, there is still some uncertainty regarding the ideal vegetation composition to mitigate CH_4 fluxes. Finally, Pelletier *et al.* (2007) found that methane flux decreased with increasing pool depth at two sites, possibly because lower sediment temperatures reduced methanogenesis (although a third site showed the opposite relationship; this was attributed to greater ebullition). A later study confirmed this result, with larger fluxes of both methane and carbon dioxide being recorded in smaller, shallower pools (McEnroe *et al.*, 2009). There is also the opportunity for methane oxidation within the water column itself (Bastviken *et al.*, 2008). Considering this, methane fluxes should be lower in deeper pools.

6.4.2. Controls on DOC

DOC concentrations were not affected by the dominant type of vegetation colonising the pools. This was somewhat expected; the upstream 'catchment' draining into each pool is typically large, flow rates are moderately high, and water residence times within individual

pools are therefore short. A direct influence of pool vegetation on DOC would thus require either rapid consumption or production of DOC within the pools, which is unlikely given the largely terrestrial source of DOC in peat drainage waters (Evans *et al.,* 2007) and the relatively recalcitrant nature of this DOC over short time periods (e.g. Wickland *et al.,* 2007; del Giorgio and Pace, 2008). Instead, it is likely that DOC will be driven by large-scale hillslope characteristics such as terrestrial vegetation cover, soil carbon pool, peat cover and hydrology (Aitkenhead *et al.,* 1999, Palmer *et al.,* 2001, Dawson *et al.,* 2004). The similarity of mean DOC concentrations among pools, down transects and in comparison to an unblocked control ditch also suggests that pools do not exert a strong influence on the processing of DOC. As a final caveat, we acknowledge that a simplified model is presented here; in reality each pool may receive water (and therefore DOC) from the peat upslope and either side of the blocked ditch, as well as from the upslope pools.

6.4.3. Zoological changes

Ditch blocking on this site created 1600 new bog pools which will enhance the habitat heterogeneity of the site (Renou-Wilson *et al.,* 2011). This large amount of standing water is likely to benefit Tipulidae species and any bird species that predate Tipulidae (Carroll *et al.,* 2011). On the spot observations supported zoological changes, with the pools being used by invertebrates such as diving beetles (genus: *Dytiscus*), whirligig beetles (family: Gyrinidae), and pond skaters (family: Gerridae). The frog species *Rana temporaria* was regularly sighted in pools, and there was evidence that *Lagopus lagopus scotica* (red grouse) used the pools for drinking/feeding.

6.4.4. Implications for restoration

Taken as a whole these findings suggest that ditch blocking can be used as a suitable restoration technique to create vegetated bog pools. After eighteen months the mean vegetation cover was 76%. However, there is potential for the pools to gradually paludify in the long term (Lindsay, 2010) and for succession to lead to the growth of species such as *Calluna vulgaris*, *Vaccinium myrtillus*, *Erica tetralix*, and *Empetrum nigrum*. On the other hand, further *Sphagnum* growth may occur, and long-term monitoring is essential to determine if this is the case. At the site studied here, the creation of bog pools was not a specific restoration objective, but has emerged as a positive side-effect that has increased the biodiversity of the ecosystem.

To ensure that the restoration achieves the best result in terms of the peatland greenhouse gas balance, our results suggest that pools should be deeper than 0.5 m. This will limit the invasion of *Eriophorum* which might otherwise result in large methane fluxes. Lavoie *et al.* (2003) however, point out that restoration activities that result in large areas of *Eriophorum* are not necessarily failures, as a process of vegetation succession has been initiated; this may lead to *Sphagnum* colonisation within 5-10 years (Lindsay, 2010). Deeper pools should also provide a less favourable environment for methanogenesis, and will lead to a longer upward travel time for methane, and hence greater opportunity for methane oxidation, dependent on the oxygen concentration profile of the pool. Neither biotic nor abiotic pool characteristics were associated with DOC concentrations and thus pool creation can be focussed on the balance between carbon cycling, vegetation colonisation, and zoological diversity.

6.4.5. Conclusions

Our survey of 60 bog pools created through ditch blocking shows that vegetation colonisation has been rapid and extensive. Plant species displayed clear environmental preferences, with *Eriophorum* colonising shallow pools and pool margins, and *Sphagnum* growing in deeper pools. No relationship could be found between any pool characteristic and DOC concentration, and we therefore suggest that restoration should aim to create deeper pools to give the greatest carbon b
enefit.

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The effect of ditch blocking on peatland methane fluxes

7.1. Introduction

Northern peatlands store approximately 547 Pg of carbon (Yu *et al.*, 2010) but they are under-represented in the Ramsar Convention that was developed to promote conservation and sustainable use of wetlands (Rubec, 1996). The Intergovernmental Panel on Climate Change (IPCC) currently only provides a cursory treatment of peatlands (IPCC, 2006), although this is now being addressed with new guidance being produced for a 2013 report. Smith *et al.* (2004) estimate that northern peatlands have been net sinks of CO_2 for around 10,000 years, as well as sources of methane (CH_4). Although CH_4 only has an atmospheric lifetime of 12 years (compared to up to 172 years for CO_2) it is the more potent GHG of the two and over one hundred years it has a global warming potential (GWP) twenty-five times that of CO_2 (Forster *et al.*, 2007). Due to their different lifetimes, comparisons of the two gases are problematic on the timescales over which peat formation takes place, and alternatives to the GWP method have therefore been proposed for peatlands (Frolking *et al.*, 2006). Nitrous oxide (N_2O) is the third major greenhouse gas, with a very high GWP, but emissions from unfertilised bogs are generally low (Moore, 1994).

The draining of peatlands through the digging of ditches can affect the hydrology and vegetation of a site (Stewart & Lance, 1991, Bellamy *et al.*, 2012). There is some evidence to suggest that if ditches are not maintained they will naturally infill (Holden *et al.*, 2007), but those on steeper slopes often continue to erode down to bedrock (Painter *et al.*, 1974). Drainage results in changes to the peatland biogeochemistry. Pristine peatlands are generally net sinks of carbon (Limpens *et al.*, 2008, Bridgham *et al.*, 2006, Worrall *et al.*, 2003, Rivers *et al.*, 1998) but can be net sources during some years (Waddington & Roulet, 2008, Roulet *et al.*, 2007). Peatlands tend to become net sources during drought years, due to the greater aeration of the peat matrix which leads to a sustained net source of CO_2 (Rowson *et al.*, 2010, Salm *et al.*, 2009). Generally, drainage and drought decrease CH_4 emissions and increase CO_2 and N_2O emissions (Alm *et al.*, 1999, Martikainen *et al.*, 1995, Glenn *et al.*, 1993, Freeman *et al.*, 1993).

CH_4 fluxes change following drainage because methanogenesis (the formation of CH_4 by archaea) is an anaerobic process in the degradation of organic matter (Garcia *et al.*, 2000), whilst methanotrophy (the ability of bacteria to metabolise CH_4 as their sole source of energy and carbon) is an aerobic process (Hanson & Hanson, 1996). The decrease in CH_4

production following water table drawdown occurs as exposure to oxygen reduces production rates (Freeman *et al.*, 2002) and increases methane oxidation rates, as methanotrophs can survive under anaerobic conditions (Blodau & Moore, 2003). Additionally, aerobic degradation in the unsaturated layers reduces substrate availability for methanogenesis; the degradation utilises carbon that would stimulate methanogensis in anaerobic conditions (Kettunen *et al.*, 1999). CH_4 oxidation also occurs and can equilibrate to a steady state just days after drainage (Blodau & Moore, 2003).

Although CH_4 fluxes from drained peatlands are often considered to be low, or zero (e.g. IPCC, 2006), a number of studies have shown that the ditches created during drainage can themselves become significant CH_4 sources (Best & Jacobs, 1997, Sundh, *et al.,* 2000, Hendriks *et al.*, 2007), contributing 60-70% of total emissions in one study (Schrier-Uijl *et al.*, 2010), and over 84% in another (Teh *et al.*, 2011). This can remain an insignificant contribution to the net carbon balance (Minkkinen *et al.*, 1997) but only when there is a large spacing between ditches and/or where net CO_2 fluxes are large. Where the space between ditches is small, drainage may actually result in a net increase in CH_4 fluxes compared to undrained sites (Roulet & Moore, 1995). There is a lack of direct information on the contribution of ditches on other systems. UK blanket bogs have been intensely drained, and the space between ditches can be <10m, but it is not well established whether these function as significant CH_4 sources in the same way as those studies undertaken in other peatland types. Cooper *et al.* (2013) found that a ditch on a Welsh blanket bog displayed low CH_4 fluxes and attributed this to: 1) water rapidly flowing along the ditch, thus limiting the potential for methanogenesis to occur, and; 2) a limited supply of substrate for methanogenesis. Contrary to this, a study of natural gullies on English blanket peat found them to be significant hotspots of CH_4 flux (and CO_2 respiration fluxes), contributing 95.8% of net CH_4 flux despite covering just 9.3% of the land (McNamara *et al.,* 2008). Similar results may be found for ditches, depending on the degree of revegetation that has occurred, water flow rate, redox status, the rate of substrate input, and other such variables, but more studies from blanket bogs are clearly needed, as it seems possible that the reduction in CH_4 emission following drainage may have been overestimated.

By attempting to raise the water table to its original level, restoration aims to return greenhouse gas (GHG) cycling towards that of an intact peatland. For CO_2, restoration usually leads to decreased total respiration (Urbanová *et al.,* 2011, Tuittila *et al.*, 1999) due to the restoration of anaerobic constraints on decomposition, and closure of the enzymic latch mechanism (Freeman *et al* 2001a), thereby creating a new CO_2 sink (Waddington *et al.*,

2010, Komulainen *et al*., 1999, Tuittila *et al.*, 1999). Whilst this change in CO_2 dynamics may occur for ombrotrophic bogs and for natural fens, restoration of other, more altered systems may produce different results; for example, rewetting an extensive peat grassland would potentially lead to decreased gross primary productivity (Beetz *et al.,* 2013). Following rewetting CH_4 fluxes rapidly increase, but, depending on how a site responds to raised water levels, sometimes remain lower than those from pristine sites (Komulainen *et al.*, 1998). When this occurs it may be due to the delayed recovery of the methanogenic community following population declines caused by long-term exposure to lowered water levels (Shannon & White, 1994), although significant increases in both methanogenesis and the methanogen populations have been observed just three months after rewetting (Urbanová *et al.*, 2011). Francez *et al.* (2000) noted a lag time in microbial response: upon rewetting methanogenesis only occurred at a peat depth of 75cm, which was assumed to be the depth of the pre-restoration water-table. Kettunen *et al.* (1999) hypothesised that methanogens and methanotrophs remain attached to peat particles and thus reside in the same layer of the peat despite water table fluctuations. Other explanations include the release of sulphate (that is generated during dry conditions) upon rewetting and the stimulation of sulphate-reducing bacteria which competitively inhibit methanogens (Freeman *et al.,* 1994, Dise & Verry, 2001).

There are effects on CH_4 flux from a purely hydrological viewpoint; pulses of CH_4 (and N_2O) have been observed within a matter of days due to the disturbance generated by the shifting water table (Hughes *et al.,* 1999, Dinsmore *et al.,* 2009), and ponds often become important CH_4 hotspots (Waddington & Day, 2007). Even if water table fluctuations are not completely curtailed following restoration (e.g. Lucchese *et al.,* 2010, Holden *et al.*, 2011) methanogenesis will still be higher in the long term, due to the increased extent of the anaerobic zone.

As previously mentioned, post-restoration CH_4 fluxes are sometimes observed to be lower than those from pristine sites. On the other hand, in other studies it has been found that CH_4 fluxes following restoration may be considerably larger than those from pristine sites. The spread in *Eriophorum* that is often observed after restoration of bogs has frequently been implicated in such a response. Some vascular plants can act as 'chimneys' by transporting gas directly to the atmosphere via their aerenchymatous tissue, and they provide substrates for methanogenesis (Marinier *et al.*, 2004). As such, numerous restoration studies have reported high CH_4 fluxes from areas of *Eriophorum* (Mahmood & Strack, 2011, Tuittila *et al.,* 2008, Marinier *et al.*, 2004, Komulainen *et al.,* 1998). Occasionally the opposite effect is

reported, and it has been hypothesised that aerenchymous tissue facilitates oxygen ingress into the rhizosphere, thus leading to decreased methanogenesis (Roura-Carol & Freeman, 1999, Dinsmore *et al.*, 2009) but this is rare. Other aerenchymatous peatland plants that have been noted to facilitate CH_4 transport include *Scheuchzeria palustris* (Shannon *et al.*, 1996), *Typha latifolia*, *Phragmites australis* (Käki *et al.*, 2001), *Juncus effusus* (Dinsmore *et al.*, 2009), and *Carex* species (Morrissey *et al.*, 1993). Considering plant species that can reduce CH_4 fluxes, it has been shown that *S.cuspidatum* can consume methane through symbiosis with methanotrophs (Raghoebarsing *et al.*, 2005). This mechanism is globally prevalent (Kip *et al.*, 2010), and not just restricted to *Sphagnum* species: *Scorpidium scorpioides*, a submerged brown moss occurring in fens and upland minerotrophic flushes, also forms this symbiosis (Liebner *et al.*, 2011).

Most of the restoration studies discussed here are of harvested sites where peat and vegetation has been extracted (Tuittila *et al.*, 1999, Francez *et al.*, 2000, Waddington & Warner, 2001, Marinier *et al.*, 2004, Anderson *et al.*, 2006, Waddington & Day, 2007, Kivimäki *et al.*, 2008, Tuittila *et al.*, 2008, Lucchese *et al.*, 2010, Waddington *et al.*, 2010, Mahmood & Strack, 2011), or of sites that were formerly drained for forestry (Komulainen *et al.*, 1998, Komulainen *et al*., 1999, Silvan *et al.*, 2002, Silvan *et al.*, 2005, Urbanová *et al.*, 2011) (table 1). A handful of others have taken place where drainage has been the only disturbance: Salm *et al.* (2012) measured fluxes of CH_4, CO_2 and N_2O from multiple sites, including a bog that was drained for peat mining where subsequent activity never commenced. They noted that peat extraction had significant effects on gas fluxes, but that drainage alone had little effect, due to a lack of response in water tables. A lack of hydrological response to ditching has been recorded previously in bogs, as Price (1997) measured similar levels of soil moisture in a drained and blocked site in a plateau bog, and Rothwell *et al.* (1996) found that ditch spacing did not control soil water content. Such results are due to the low hydraulic conductivity that blanket bogs display (Galvin, 1976, McDonald *et al.*, 1991), but a lack of water table response to ditching is not found in all peatlands. For example, ditches in fens can lead to extensive lowering of the water table (Cooper *et al.*, 1998), and ditches in tropical peats lead to large and persistent drops in the water table, such that it resides below the ground surface for most of the year (Page *et al.*, 2009).

Table 1. Summary of CH_4 fluxes following ditch blocking. Studies on cutover peatlands, or experiments solely involving water table manipulations have been excluded.

	Treatment	Comparison	CH_4 change	Units
Komulainen 1998	Ditch blocking, clear cutting	Pre vs post	0.8 - 4.6	g/m/yr
Urbanová 2011	Lab incubation of soils	Pristine vs drained	0.0006 - 0.0060	µmol/g/hr
Green 2011	Lab incubation of cores	No infill vs *Sphagnum* infill vs heather bale vs reprofiling	-0.23 - 15.2 - 7.2 - 12.8	g/m/yr
Cooper 2013	Ditch blocking	Drained vs blocked	4.9 - 16.3	g/m/yr

In the UK there is much uncertainty concerning the exact size of the peatland carbon store, but just over 3 Pg has been estimated as a minimum value (Lindsay, 2010). Considering that blanket bog comprises 87% of all UK peatland (Baird *et al.*, 2009) there is a clear knowledge gap regarding GHG fluxes following ditch blocking on blanket bog (Baird *et al.*, 2009, Lindsay, 2010,). A mesocosm experiment subjecting peat cores from blanket bog to simulated ditch blocking techniques found that CO_2 fluxes were largest when heather bales were used, and smallest when *Sphagnum* species colonised after blocking (Green *et al*., 2011). CH_4 fluxes were larger under reprofiled treatments (see section 2.1), heather bale dams, and damming followed by *Sphagnum* colonisation, compared to dams with pools behind. The authors expressed the caveat that these results may be misleading, as in reality pools will receive water and DOC inputs from surrounding peat which may have implications for CH_4 emissions (Green *et al*., 2011). The only controlled field ditch-blocking study on blanket bog to date (Cooper *et al.*, 2013) found that ditch blocking increased CH_4 fluxes, and that this was associated with *Eriophorum vaginatum* that colonised the blocked ditch. The authors noted that this relationship was confounded by the effect of water table, and speculated that measured post-restoration decreases in sulphate concentration may have reduced inhibitions on methanogenesis. Additionally, bales of *Calluna* were used to block ditches which may have provided substrate for methanogenesis. In support of this, high concentrations of DOC have been associated with ditch blocking using *Calluna* bales (Green *et al.*, 2011).

The purpose of the study described here was to measure the effect of drainage and ditch blocking on CH_4 (and CO_2 and N_2O) fluxes on blanket bog; considering fluxes from within open and blocked ditches (including pools formed during restoration), as well as fluxes from blanket bog adjacent to ditches. A further objective was to use this dataset to extrapolate fluxes to the landscape scale to determine what effect ditch blocking had on CH_4 fluxes throughout the catchment. Monitoring commenced several months before ditch

blocking took place to provide baseline data, and a number of ditches were left unblocked to act as experimental controls. This allowed a direct comparison of ditched and ditch-blocked treatments. Any effects of drainage on fluxes could only be inferred, as the experiment did not include a pre- and post-comparison of pristine vs drained bog. It was hypothesised that drainage would have reduced CH_4 fluxes, whilst ditch blocking would lead to increased CH_4 fluxes due to the raised water table, with pools being particular hotspots.

7.2. Materials and Methods

7.2.1. Study site

The study was carried out at the head of the Afon Ddu catchment (latitude 52.97°N, longitude 3.84°W) on the Migneint blanket bog, in Snowdonia National Park, north Wales (UK). The altitude of the catchment ranges from 490 m ASL with a mean peat depth of 1.32 m. Dominant vegetation is *Calluna vulgaris*, *Eriophorum*, *Juncus* and *Sphagnum* species, as well as *Erica tetralix*, *Vaccinium myrtillus*, *Empetrum nigrum*, and *Vaccinium vitis-idaea*. Twelve adjacent ditches that run directly downslope in a north-northwest direction were selected. The ditch spacing is 10-20 m. Ditch blocking throughout the catchment took place in February 2011. Four ditches were left open as controls, and eight were blocked using two different methods. Four were blocked using peat dams, where the peat is extracted from 'borrow pits' adjacent to the ditch. The remaining four were blocked using a reprofiling technique. This involves the ditch vegetation being removed, and the peat bottom being compressed to destroy any natural pipes that may be present and hydrologically active. The ditch is then infilled with peat and the vegetation is replaced. As in the previous treatment peat dams are also constructed along the ditch.

7.2.2. Static chamber CH_4 and N_2O gas sampling

Fluxes were measured using the static chamber method (Livingston & Hutchinson, 1995) with opaque chambers. Thirty six cylindrical polyvinyl chloride collars were installed in June 2010. These were 30 cm in diameter and 20 cm in height. Four 10 mm holes were drilled into the bottom of each collar (i.e. that part that would be underground) to prevent water pooling. Collars were inserted into the peat to a depth of 10 cm. Each ditch had three collars associated with it; one collar within the ditch, one collar 1 m west of the ditch, and one collar 3 m west of the ditch. Two 10 mm holes were drilled into the above-ground portion of ditch collars to allow water to flow through them. These were sealed with rubber bungs during gas sampling. Collars were removed approximately ten days before ditch

blocking took place, and were reinstalled approximately ten days after ditch blocking in the same locations. Within-ditch collars for blocked treatments were reinserted as close to their original position as possible. These original collars allowed a direct pre- and post- rewetting treatment comparison.

In June 2011 additional collars were installed, as the restoration activity results in some variation in the location of the original collars that might bias results (i.e. some collars were just upslope of dams, some were just downslope of dams). For all ditches new collars were installed as per the original collar layout (i.e. one within-ditch and two adjacent to the ditch). The exception was ditch 5 as the original collars were deemed to be in a satisfactory position. For each open control ditch, one within-ditch collar was on bare peat, and one was on an area of naturally re-established *Sphagnum*. As well as the new collars, a pool behind a dam was selected for each of the eight blocked ditches. At each pool, four canes were used to mark an area where a floating static chamber was used to measure pool fluxes. These secondary collars were used to compare blocked ditches against control ditches (fig. 1 & 2).

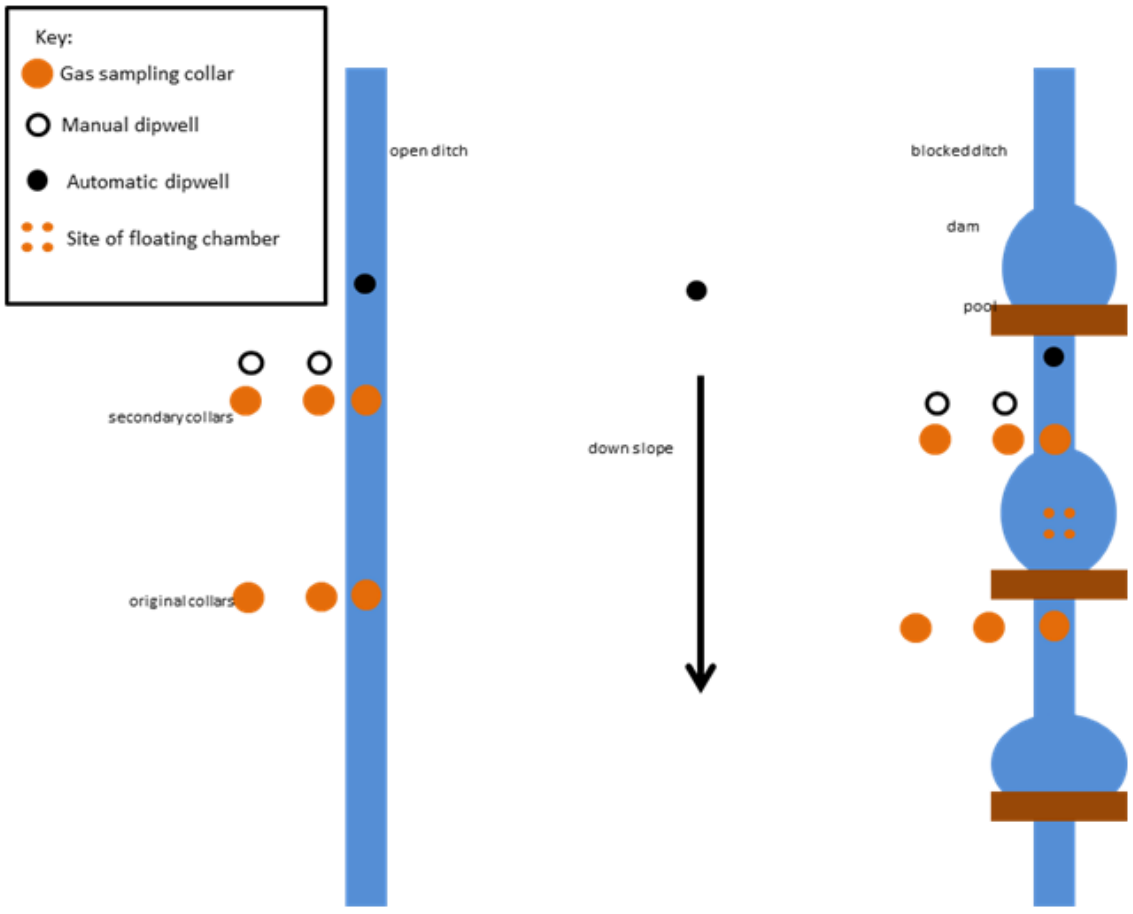

Figure 1. Schematic of two ditches (one unblocked, one blocked) showing the gas sampling collars and dipwells (not to scale)

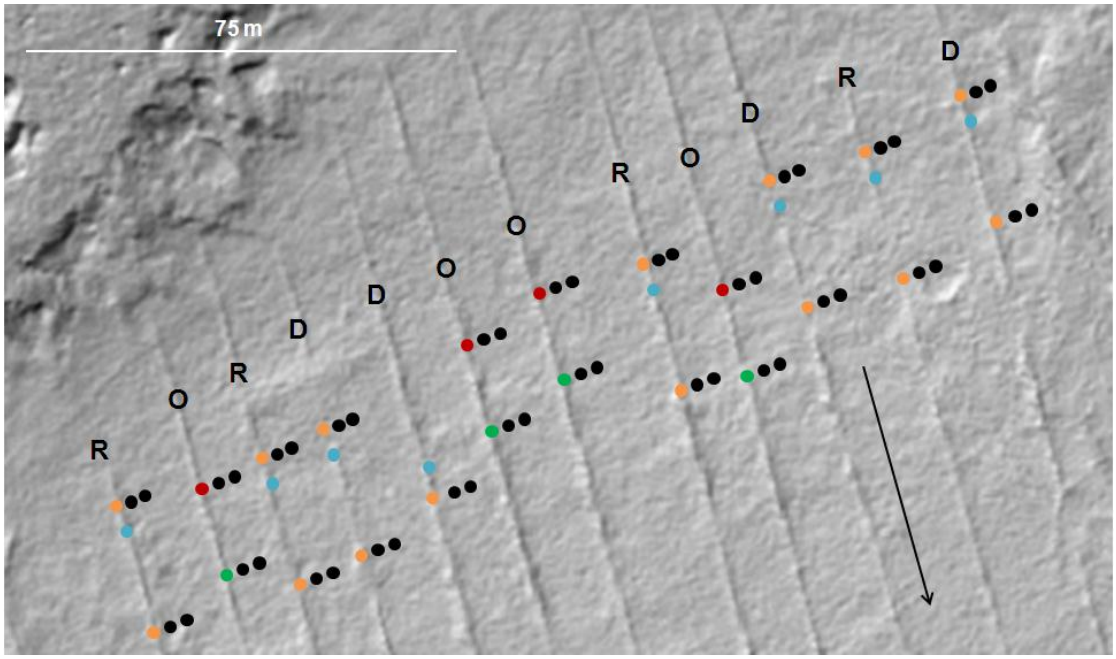

Figure 2. LIDAR image of the experimental site, taken before rewetting. R, O and D indicate reprofiled, open/control, and dammed ditches respectively. Circles represent collars (not to scale). Black = collars 1m and 3m adjacent to ditches. Orange = collars within blocked ditches. Blue = floating chambers in blocked ditches. Green = collars on *Sphagnum* in open ditches. Brown = collars on bare peat in open ditches. Arrow points downhill. Secondary collars are those further up slope, whilst original collars are those downslope.

Static chambers were originally constructed using bell-shaped cloches made from injection moulded high grade UV-stabilised plastic (Haxnicks, UK) attached to sections of the same polyvinyl chloride that the collars were made from. They were sealed using neoprene foam. When the new collars were inserted a new chamber design was used, consisting of an acrylic cylinder with a flat top. A new sealing method was used by attaching a small plastic gutter to the top of the collar which could be filled with water. The chamber slotted into this water to create a seal. Chambers were covered in silver radiator foil to reduce temperature fluctuations. Both chamber designs featured a small electric fan attached to the top of the chamber to ensure complete gas mixing. Additionally, a short acrylic tube protruded through the chamber wall with a balloon attached on the inside to allow pressure equalisation between the inside and outside of the chamber. Temperature, pressure and humidity inside the chamber were monitored with a Commeter C4141 probe (Comet Systems, Czech Republic). A septum in the chamber wall allowed gas samples to be extracted. To sample fluxes from pools, a floatation device was attached to the same chambers using either an inflated rubber inner tube or a piece of foam.

Gas samples were extracted using disposable syringes fitted with 21 gauge needles. Five samples were taken per chamber, at 0, 5, 10, 15 and 20 minutes. Each extraction was preceded by triplicate purges of the syringe with the needle penetrating through the septum into the chamber. For samples from July 2010 to January 2012, 25 ml of sample was extracted and transferred into 22 ml vials (Perkin Elmer, USA) that had been pre-evacuated by hand. For samples from March 2012 onwards 15 ml of sample was extracted and transferred into 12 ml vials that had been mechanically pre-evacuated (Labco, UK). Samples were analysed for CH_4 and N_2O using a gas chromatograph (GC) fitted with a flame ionisation detector (FID) and electron capture detector (ECD). July 2010-January 2012 samples were analysed on a Perkin Elmer Clarus 500 GC, and March 2012 samples onwards were analysed on a Varian 450 GC. Standard analytical grade reference gases (Cryoservice, UK, or Scientific and Technical Gases, UK) were used for calibration and to check for drift.

Sampling took place on a monthly basis from July 2010 to August 2012. The order of sampling of static chambers changed on each sampling occasion so as to remove any potential bias from diurnal patterns in temperature. At each collar, soil temperature at 10 cm was measured using a CheckTemp Electronic Thermometer (Hanna Instruments, UK). Each set of collars associated with each ditch was equipped with a piece of lightweight boardwalk which could be placed before each collar to reduce researcher-mediated artefacts (e.g. CH_4 ebullition events due to extra weight on the peat surface). Samples were analysed within one week of collection.

7.2.5. Flux calculations

Fluxes were calculated according to Denmead (2008), using the modified formula:

$$F_g = \frac{1}{A}\frac{dg_m}{dt} \qquad \text{(Equation 1)}$$

where F_g is the gas flux density at the peatland surface (M L^{-2} T^{-1} – mg m^{-2} day^{-1}), A is the area inside the collar (L^2 – m^2), g_m is the mass of gas in the chamber (M – mg), and t is time (T – days). g_m was calculated as:

$$g_{m=V \times \rho_g} \qquad \text{(Equation 2)}$$

where V is the combined volume of the static chamber and the above-ground section of the collar, and ρ_g is the mass concentration of gas in the chamber (M L^{-3} – mg m^{-3}). An ordinary least squares linear regression was fitted through the mass and time data to give the rate of increase or decrease in gas mass. If the gradient of the linear regression was found to be

significant ($p < 0.05$) and $r2 > 0.7$ the flux (F_g) was then calculated. Data for some chambers passed these criteria but displayed high initial gas concentrations followed by a steady concentration increase. This was attributed to steady ebullition and removed from the analysis. Some chambers displayed high initial gas concentrations followed by a decline in concentration. This was attributed to an ebullition event and subsequent bubble mixing, and these data were removed from the analysis. If the change in concentration within the chamber was < 0.3 ppm then no flux was deemed to have occurred (i.e. zero flux). Any data that did not meet the criteria for flux or zero flux was removed, e.g. due to episodic ebullition occurring midway through chamber deployment (Green & Baird, 2011).

7.2.6. Static chamber CO_2 gas sampling

A limited number of CO_2 fluxes were measured using an EGM-4 infra red gas analyser (PP Systems). Field campaigns too place in summer 2011 and 2012. Respiration (i.e. dark chamber fluxes) was measured on four occasions. On three occasions in summer 2012 both dark and light chamber fluxes were measured and therefore net ecosystem exchange (NEE) could be calculated. The IRGA was typically deployed for approximately two minutes on each collar, as this generally allowed a linear flux to be observed.

7.2.7. Water table measurement

Water tables were measured using dipwells. Automated dipwells were situated on the peat equidistant between each pair of ditches. They were equipped with WT-HR 1000 data loggers (TruTrack, New Zealand) recording every 2 hours. Dipwells were removed approximately ten days before ditch blocking took place, and were reinserted approximately ten days after ditch blocking. Additional dipwells were installed in June 2011, and these were placed besides each of the new (none-ditch) gas sampling collars that were installed that month. These additional dipwells were monitored manually, and a water table reading taken on each gas sampling trip. Figure 1 shows dipwells as part of a schematic of part of the field site.

7.2.8. Statistics

Statistical analysis was performed using SPSS v20 (IBM Corporation, http://www-01.ibm.com/software/analytics/spss/products/statistics/). After testing for normality, ANOVAs or Kruskal-Wallis tests were used. Tukey HSD post-hoc tests were used with ANOVAs. After significant Kruskal-Wallis tests, Mann-Whitney tests were used to

determine between which groups significance was found. Chi-square was used to test the association of vegetation/collar type and the incidence of negative flux.

7.3. Results

7.3.1. N_2O fluxes

Fluxes of N_2O were below the detection level of the GC throughout the study, and are therefore not presented. This is frequently observed for blanket bogs (e.g. Wilson *et al.*, 2013).

7.3.2. Pre-rewetting differences

During the pre- rewetting period (July 2010 – January 2011), all ditches were unblocked and therefore data could be pooled for analysis (note however that the measurements do not cover a full year) (fig. 3). Mean CH_4 flux from within-ditch collars was 11.6 mg CH_4 m^{-2} d^{-1}, and the major contribution to this flux came from ditches that were subsequently dammed. Kruskal-Wallis/Mann-Whitney tests showed this to be significantly higher than collars 1 m next to the ditch, where mean flux was 4.3 mg CH_4 m^{-2} d^{-1}. There was no significant difference between fluxes from collars 3 m from ditches (mean of 8.0 mg CH_4 m^{-2} d^{-1}) and fluxes from ditch collars. Additionally, there was no significant different between fluxes from collars 3 m from ditches and collars 1 m from to ditches. Highest mean monthly fluxes during the pre- rewetting period were observed in July and August (15.3, 12.7 and 21.5 mg CH_4 m^{-2} d^{-1} for ditch, 1 m and 3 m collars respectively). Lowest mean monthly fluxes were more widely distributed and were observed in January, September and November (8.2, 0.7 and 1.9 mg CH_4 m^{-2} d^{-1} for ditch, 1 m and 3m collars respectively).

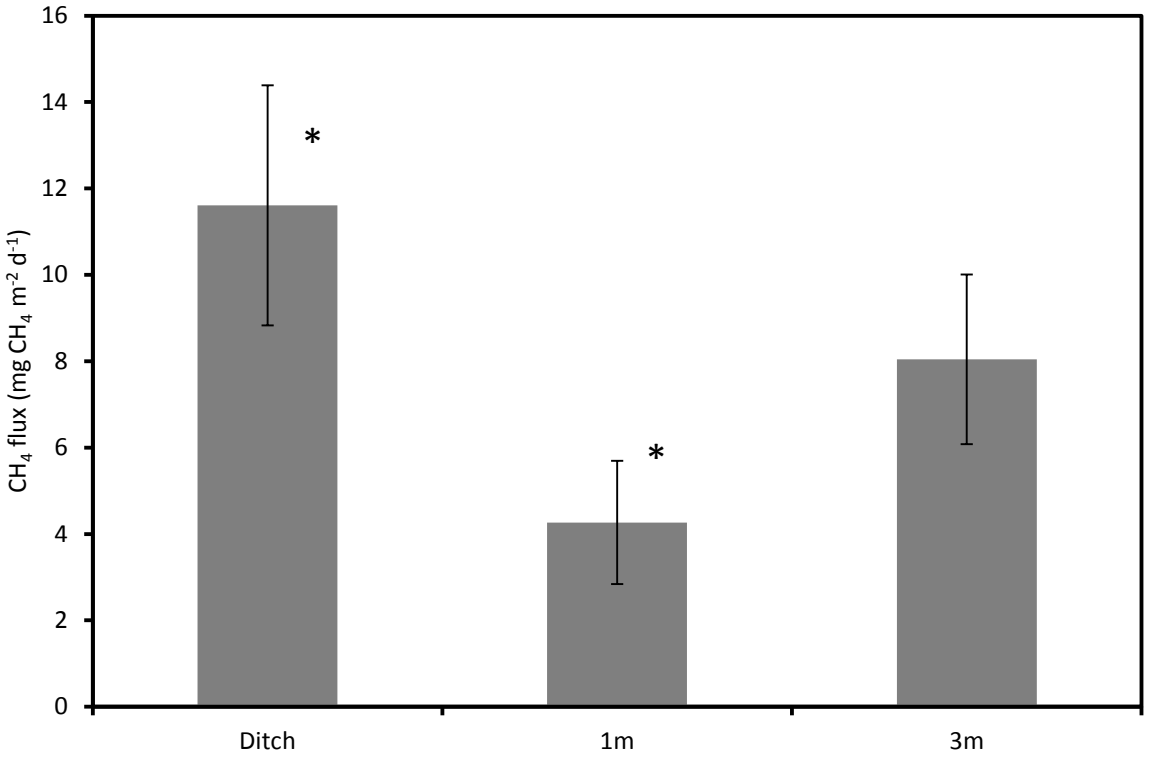

Figure 3. Mean CH_4 flux for all 12 ditches in the pre-rewetting period. Bars represent means for all pre-blocking sampling dates from original ditch collars, collars 1 m adjacent, and 3 m adjacent to ditches. *n* = 39, 46, and 42 respectively. Error bars show standard error of the mean. Significant differences are marked by *.

7.3.3. Effect of ditch blocking on water tables

Automatic dipwells were installed mid-way between ditches, therefore did not strictly belong to either blocked or unblocked treatments; that is, they were potentially influenced by the two ditches either side. However, grouping the dipwells into those where the water table had been 'fully-restored' (i.e. ditches on either side had been blocked) and 'half-restored' (i.e. the ditch to one side had been blocked, and the ditch to the other left open) allowed a simple comparison to be made. This showed that the depth from the peat surface to the water table was, on average, greater for the dipwells monitoring half restored bog, but that this difference existed before blocking. A t-test showed that the pre-blocking difference between fully-restored and half restored bog was not significant, whereas post-blocking it was significant ($p<0.01$, fig. 4).

Manual dipwells that were installed adjacent to collars (1 m and 3 m from ditches) after blocking took place showed that the depth to the water table was greater for collars next to open ditches. Mean depth to water table was 9.2 cm for unblocked control ditches, 7.7 cm for dammed ditches, and 7.2 cm for reprofiled ditches. ANOVA showed that this difference

was significant between control ditches and reprofiled ditches ($p<0.05$), but the difference between control ditches and dammed ditches was only significant at a weaker level ($p<0.1$) (fig. 5).

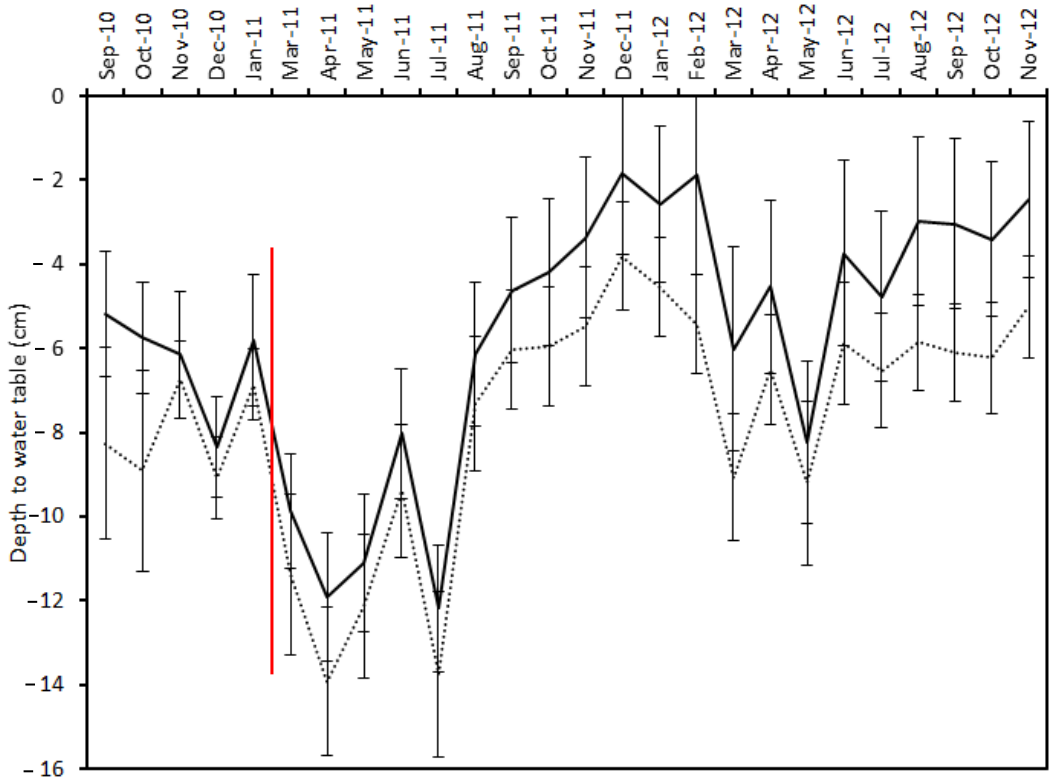

Figure 4. Monthly mean depth to water table for restored (continuous line) and half restored (dotted line) blanket bog. For each month number of dipwells is usually $n = 5$ for restored and 6 for half restored. Error bars show standard error of the mean. Red line indicates when ditch blocking took place. The pre-blocking difference is not significant, whereas the post-blocking difference is significant.

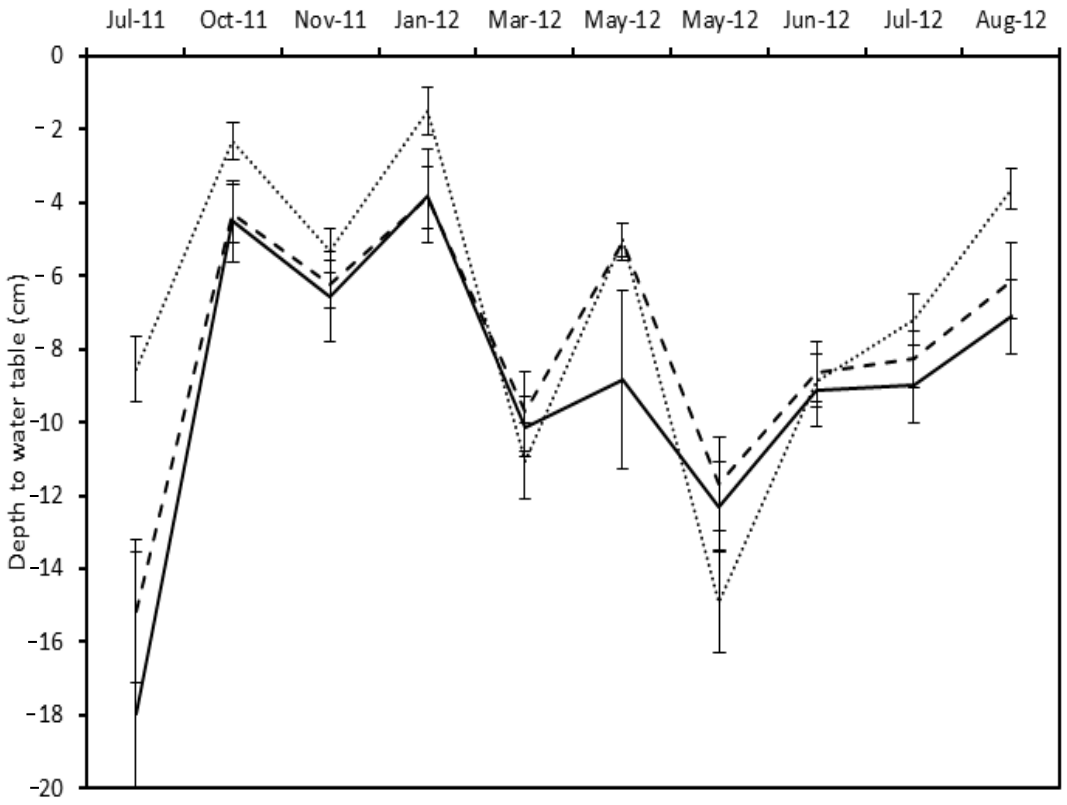

Figure 5. Monthly mean depth to water table for dipwells associated with collars for unblocked control ditches (continuous line), dammed ditches (dashed line) and reprofiled ditches (dotted line). For each month number of dipwells is $n = 8$ for each treatment. Error bars show standard error of the mean. There were sampling trips in both early and late May, hence the duplication on the x axis. The difference is significant between control ditches and reprofiled ditches ($p<0.05$), but the difference between control ditches and dammed ditches is only significant at a weaker level ($p<0.1$)

7.3.4. Effect of water table on CH_4 flux

Manually operated dipwells were installed alongside secondary (post-blocking) collars to provide paired CH_4 flux and water table data. It is frequently difficult to attribute variability in CH_4 fluxes measured using static chambers to environmental variables (Levy *et al.*, 2012), and therefore averaging data is often desirable to reduce noise and elucidate patterns (Cooper *et al.*, 2013). By grouping fluxes according to water table level (using 1 cm increments) a negative relationship was found between water table and CH_4 flux. Linear regression showed that there was a negative relationship between the two variables, i.e. that as the water table drops further from the surface CH_4 flux decreases (fig. 6). At the highest observed mean water table depth of 21 cm, this regression suggests that the CH_4 flux was around 25% of that observed when water table was at or above the ground surface.

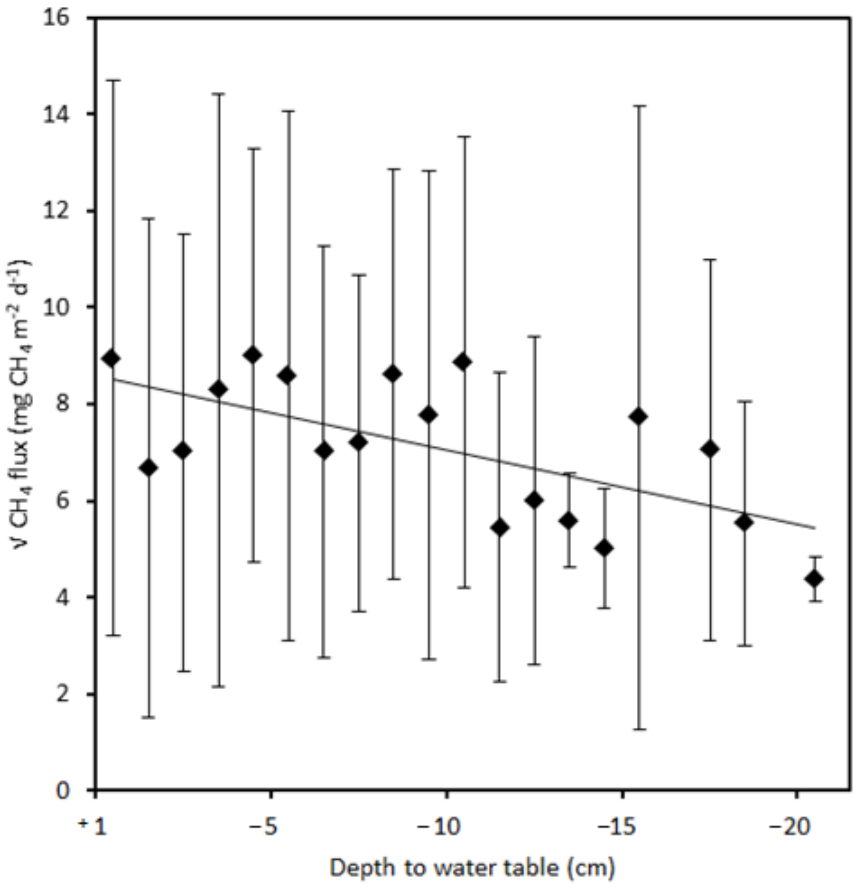

Figure 6. Mean CH_4 flux (square root transformation) for varying water table depths. $r^2 = 0.40$, $p<0.05$. Error bars show standard error of the mean.

7.3.5. Pre- and post-rewetting treatment comparison

The originally-installed collars were used for a direct pre- and post- rewetting comparison. Before analysing post- rewetting fluxes, pre- rewetting data were compared according to their assigned future treatments to determine whether any pre-existing difference in fluxes existed. There was no significant difference between groups for collars 1 m and 3 m from the ditch. However, there was a significant difference for within-ditch collars between those assigned to reprofiled and dammed ditches. The difference between means was 20.4 mg CH_4 m^{-2} d^{-1}; mean flux from reprofiled ditches was – 0.3 mg CH_4 m^{-2} d^{-1}, and mean flux from dammed ditches was 20.1 mg CH_4 m^{-2} d^{-1}.

Analysis of post- rewetting data revealed a significant difference in fluxes between open and dammed, and open and reprofiled treatments for ditch collars. There was no significant difference between treatments for collars 1 m adjacent to ditches, but a significant difference between open and reprofiled ditches for collars 3 m adjacent to ditches (fig. 7). Fig. 8 displays these data as a time series. Rewetting resulted in moderate increases in fluxes

from dammed blanket bog approximately four months post-blocking, which were followed three to five months later by extremely large flux increases from reprofiled blanket bog. Although the CH_4 increase following ditch blocking is, to some extent, driven by high within-ditch fluxes, collars adjacent to ditches also displayed high fluxes; examples include fluxes of 291, 105, 553, and 302 mg CH_4 m^{-2} d^{-1} for reprofiled blanket bog, and 139, 107, 102, and 79 mg CH_4 m^{-2} d^{-1} for dammed blanket bog.

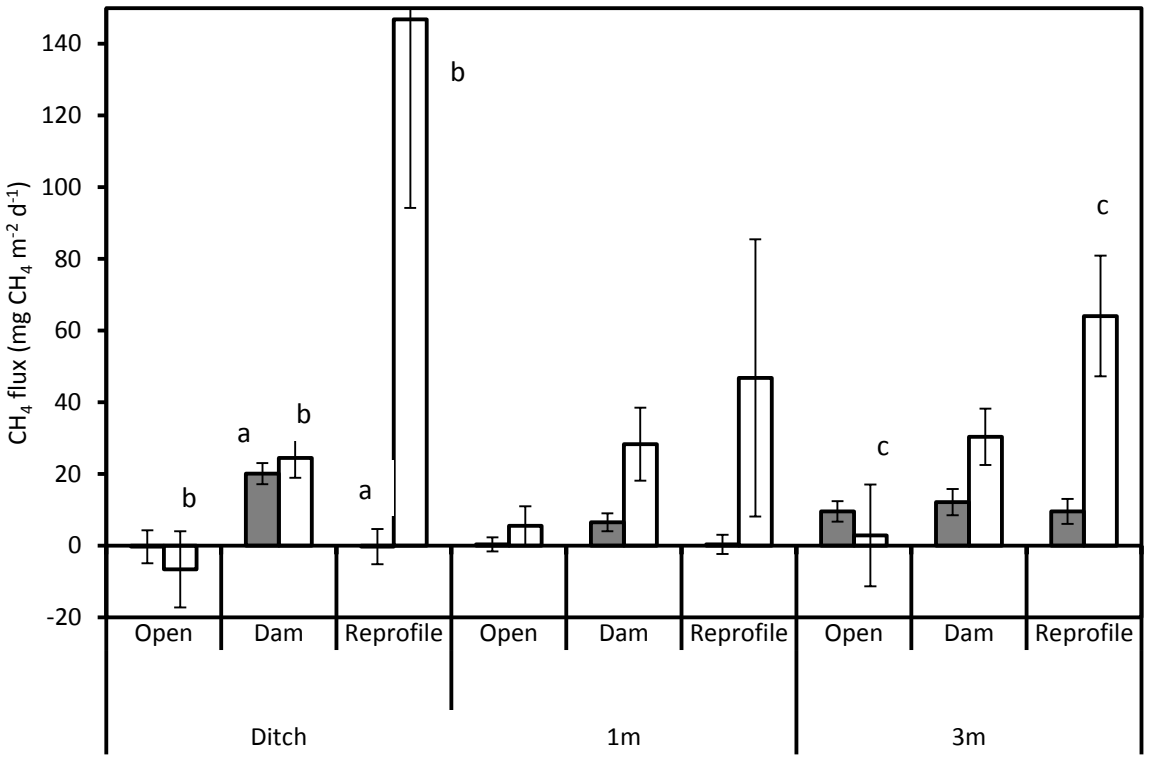

Figure 7. Pre- (filled bars) and post-rewetting (open bars) CH_4 fluxes from original collars within ditches, 1 m adjacent to ditches, and 3 m adjacent. Error bars show standard error of the mean. *n* is variable, but mean values are 14 pre-rewetting and 18 post-rewetting (see appendix for details). Note that y-axis has been truncated for clarity, so that the upper (symmetrical) error bar for the reprofiled ditch is not shown. Bars with shared letters are significantly different from each other.

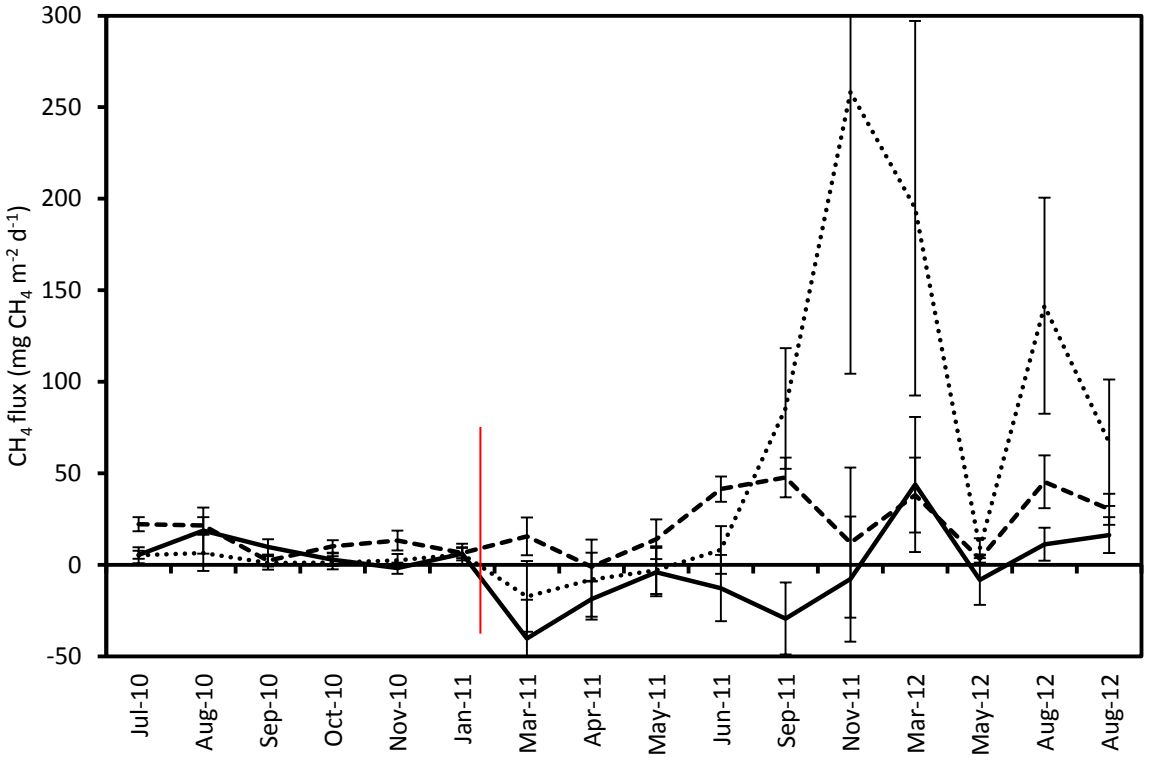

Figure 8. Monthly mean CH_4 fluxes for all original collar positions, pre- and post-rewetting, for open ditches (continuous line), dammed ditches (dashed line) and reprofiled ditches (dotted line). Red line indicates when ditch blocking took place. Error bars show standard error of the mean. *n* is variable between months and treatments, but mean for each treatment is $n = 6$ (see appendix for detail). Sampling took place both in early and late August in 2012, hence duplication of dates shown on the x axis.

7.3.6. Post-rewetting treatment comparison

Analysis of data from secondary collars suggested that ditch blocking had a significant effect on CH_4 fluxes from within ditches (fig. 9). Collars in reprofiled and dammed ditches displayed significantly larger fluxes than collars on either *Sphagnum* or bare peat in open, unblocked ditches. Floating chambers on pools in reprofiled and dammed ditches also showed significantly larger fluxes than those in unblocked ditches. Post-blocking, the highest mean flux (186.2 mg CH_4 m^{-2} d^{-1}) was associated with pools within reprofiled ditches, and the lowest was associated with bare peat in unblocked ditches (3.6 mg CH_4 m^{-2} d^{-1}). Differences between pool and ditch fluxes were not significant within either the reprofiling or damming treatments. Similarly, there was no difference in fluxes between *Sphagnum* and bare peat collars in unblocked ditches.

For all treatments, CH_4 fluxes were very similar for collars 1 m and 3 m adjacent to ditches. For both collar locations there was no significant difference between dammed and reprofiled ditches, but collars next to open, unblocked ditches showed significantly larger

fluxes (fig. 10). Combining data for all terrestrial collars for each treatment shows that reprofiled ditches had the largest overall flux, and that this was significantly higher than fluxes from dammed ditches and fluxes from open, unblocked ditches (fig. 11). There was no significant difference between dammed and open ditches

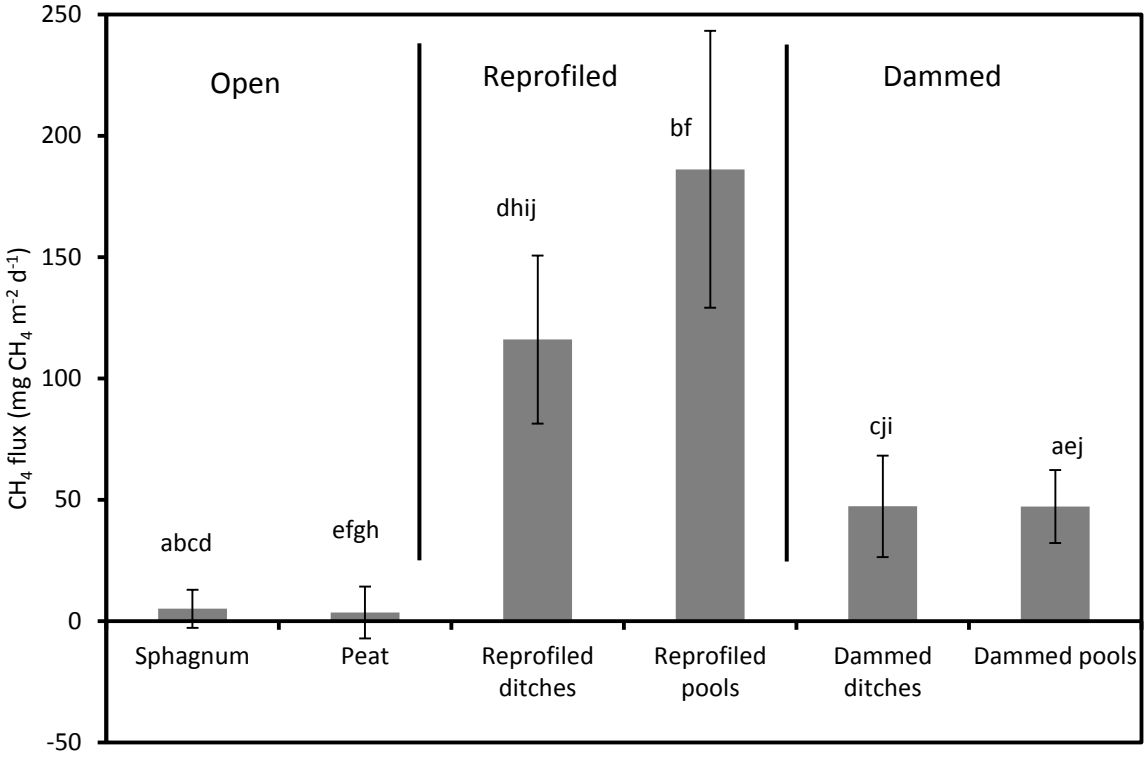

Figure 9. Mean CH_4 fluxes for all six within-ditch collar types within treatments: *Sphagnum* within unblocked ditches (n = 36), bare peat within unblocked ditches (n = 37), collars in reprofiled ditches (n = 35), floating chambers on pools in reprofiled ditches (n = 35), collars in dammed ditches (n = 33), and floating chambers on pools in dammed ditches (n = 29). Bars represent means for all sampling dates from secondary collars. Error bars show standard error of the mean. Letters mark pairs where a significant difference in CH_4 is present at $p<0.05$, except c where $p=0.052$.

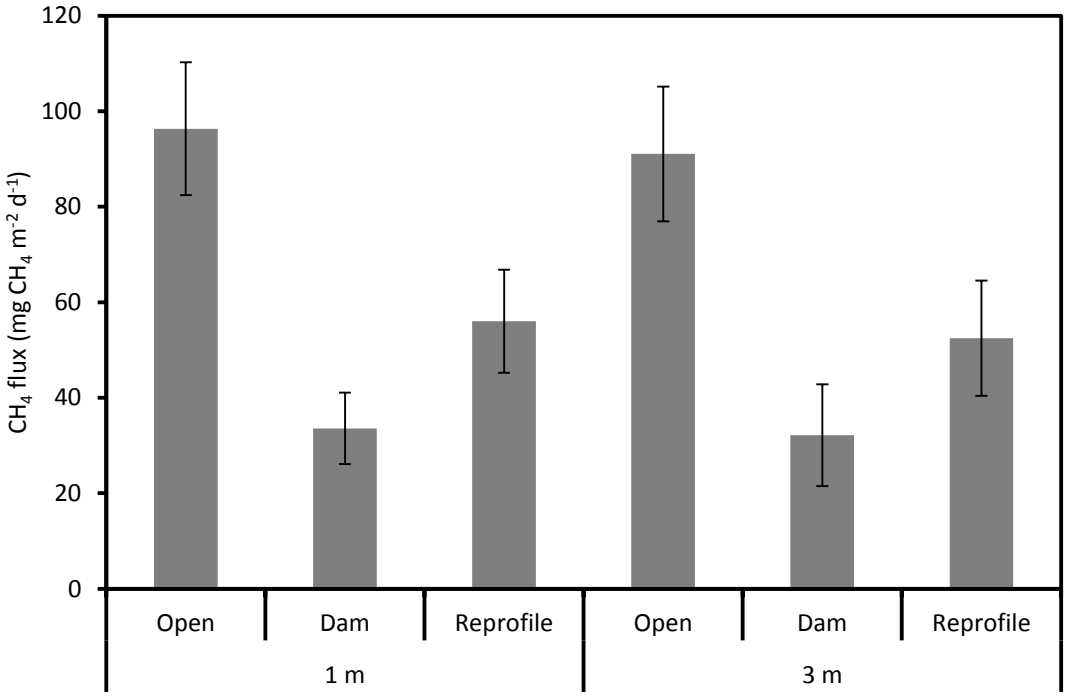

Figure 10. Mean CH_4 fluxes for collars 1 m and 3 m adjacent to ditches for each respective treatment. Bars represent means for all sampling dates from secondary collars. From left to right n = 36, 40, 48, 36, 38, and 47. Error bars show standard error of the mean. For both 1 m and 3m collars there is no significant difference between dammed and reprofiled treatments, but fluxes from open ditches are significantly higher.

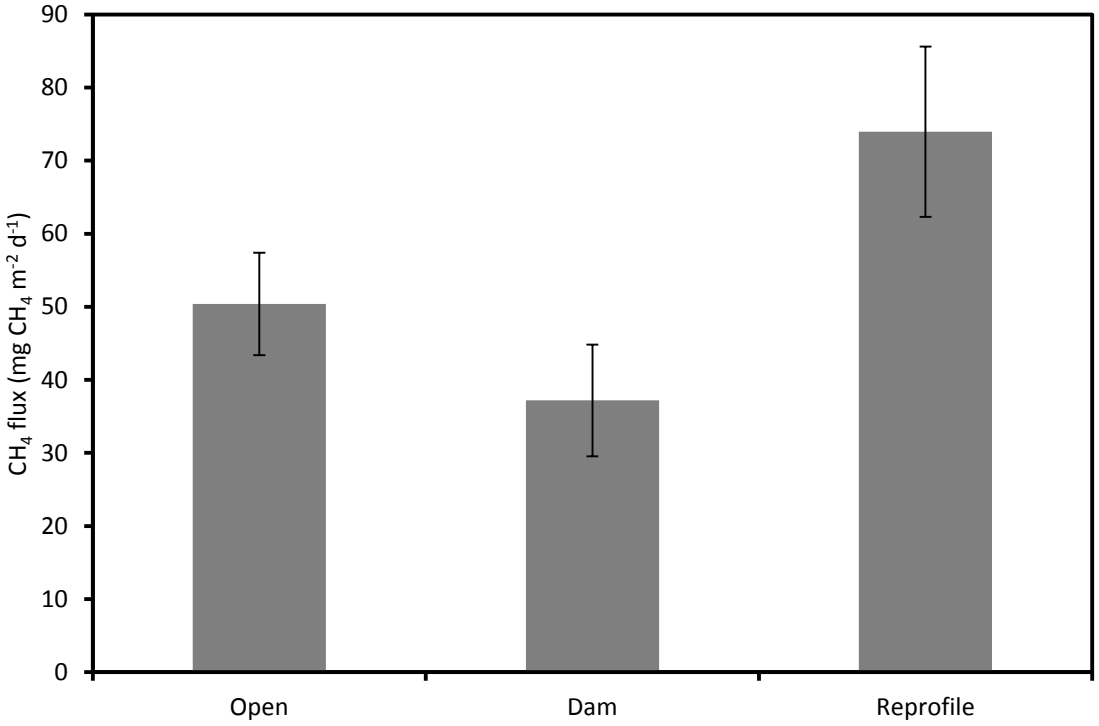

Figure 11. Mean CH_4 fluxes for all terrestrial (secondary) collars (i.e. ditch, 1 m and 3 m collars) for all sampling dates. n = 151, 111, and 124 for open, dammed and reprofiled treatments respectively. Error bars show standard error of the mean. There is no significant difference between dammed and open collars, but reprofiled fluxes were significantly higher.

7.3.7. Landscape extrapolations

Methane fluxes were calculated for the Afon Ddu catchment as follows: a catchment area of 1.59 km^2 was defined using mapping and aerial photography. Total ditch length within this catchment was estimated from aerial photography at 32.5 km. A ditch width of 0.5 m was then used to calculate the total area of ditches within the catchment. The catchment was divided into ditch area, strips of bog beside each ditch 1 m in diameter, and remaining bog, and mean fluxes for each land type upscaled accordingly (fluxes for collars at 3 m were used for the remaining bog). Before upscaling, annual fluxes for each microform were -0.1 – 4.2 g CH_4 m^{-2} yr^{-1} for open ditches, 0.1 – 2.4 g CH_4 m^{-2} yr^{-1} for bog 1 m adjacent to open ditches, and 2.9 – 4.4 g CH_4 m^{-2} yr^{-1} for bog 3 m adjacent to open ditches. Post-blocking fluxes were 8.9 – 53.6 g CH_4 m^{-2} yr^{-1} for blocked ditches, 17.2 – 67.9 g CH_4 m^{-2} yr^{-1} for blocked pools, 10.3 – 17.8 g CH_4 m^{-2} yr^{-1} for bog 1 m adjacent to blocked ditches, and 3.5 – 11.1 g CH_4 m^{-2} yr^{-1} for bog 3 m adjacent to blocked ditches. Upscaling these figures to the unblocked, drained catchment, gave a flux of 2.89 g CH_4 m^{-2} yr^{-1}. Catchment fluxes were then estimated using two scenarios: one where ditches were blocked through damming, and one where ditches were blocked through reprofiling. For both scenarios, ditches were considered in 10 m sections, each section consisting of a 1 m dam, a 2 m pool, and 7 m of blocked ditch, repeated throughout the catchment. These scenarios suggest that damming ditches increases the catchment CH_4 emission to 3.45 g CH_4 m^{-2} yr^{-1} and that reprofiling ditches increases it to 4.11 g CH_4 m^{-2} yr^{-1}. Borrow pits were then factored into flux estimates as follows: each dam was considered to have one borrow pit associated with it, of a size of 1 m by 1 m. Borrow pit fluxes were estimated as a mean of those from reprofiled pools and ditches, and this was added to the calculation. This increased post-blocking fluxes to 3.55 g CH_4 m^{-2} yr^{-1} for dammed ditches and 4.21 g CH_4 m^{-2} yr^{-1} for reprofiled ditches.

7.3.8. Other controls on CH_4 fluxes

Negative CH_4 fluxes were observed on numerous occasions (fig. 12). They were observed most frequently from collars in unblocked ditches; on 16% of occasions from bare peat and on 17% of occasions from *Sphagnum*. The lowest number of negative flux occasions were observed from pools in blocked ditches (3%). A chi-squared test showed that the association between collar location and incidence of negative CH_4 flux was significant.

After removing negative fluxes, and fluxes larger than 300 mg CH_4 m^{-2} d^{-1}, a weak but significant relationship was found between soil temperature at 10 cm and CH_4 flux. This

relationship was clarified by performing a square root transformation on the data (fig. 13). Fluxes showed more variation at the higher temperatures and thus this relationship could be clarified by taking the mean flux for each 1^{o}C temperature increase (fig. 14), where a strong, significant underlying relationship between mean CH_4 flux and temperature could be detected. This approach was similar to that taken to establish the relationship between CH_4 flux and water table, and helped to remove noise from raw data. The relationship between soil temperature and CH_4 flux was visibly evident through time (fig. 15).

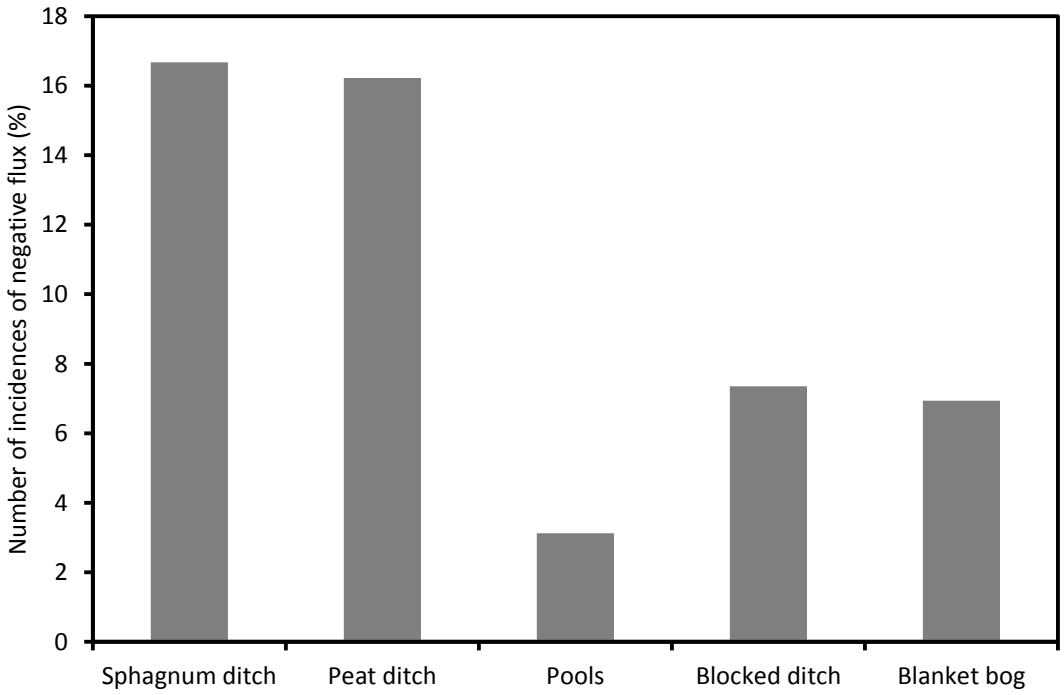

Figure 12. Percentage number of incidences of negative CH_4 fluxes observed for *Sphagnum* (n = 36) and bare peat (n = 37) in unblocked ditches, pools in dammed and reprofiled ditches (n = 64), blocked ditches (n = 68), and collars on blanket bog adjacent to blocked and unblocked ditches (n = 245). The relationship between collar location and incidence of negative flux is significant.

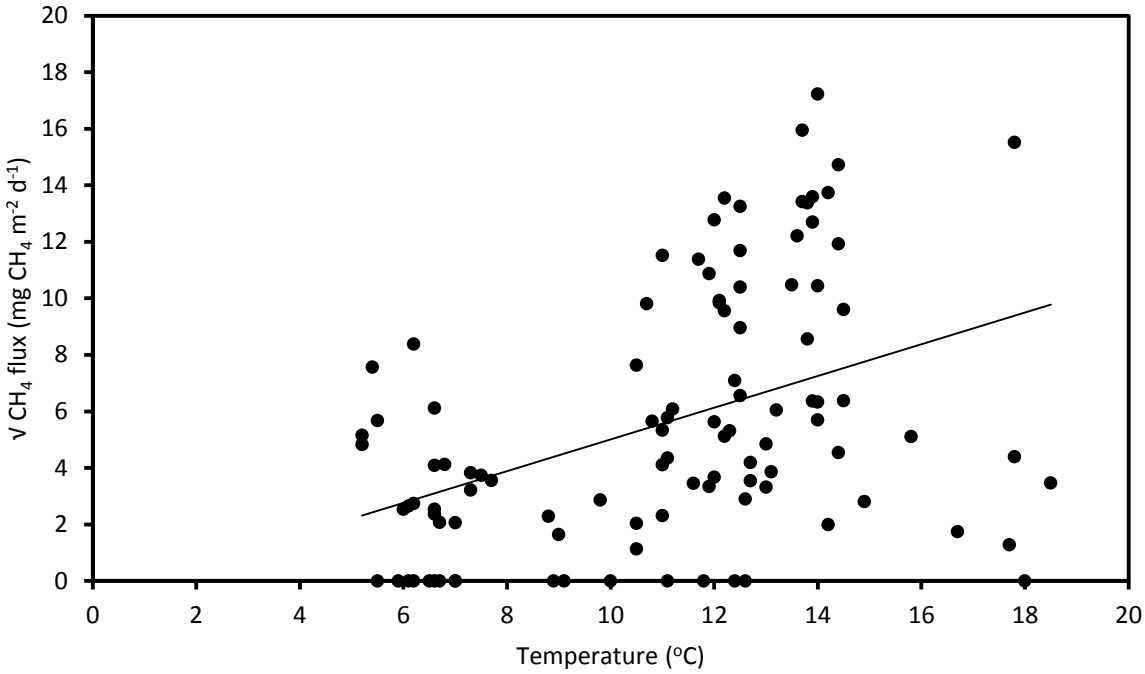

Figure 13. Relationship between soil temperature at 10 cm depth and CH_4 flux (square root transformation). *n* = 104. $r^2 = 0.17$, $p<0.05$.

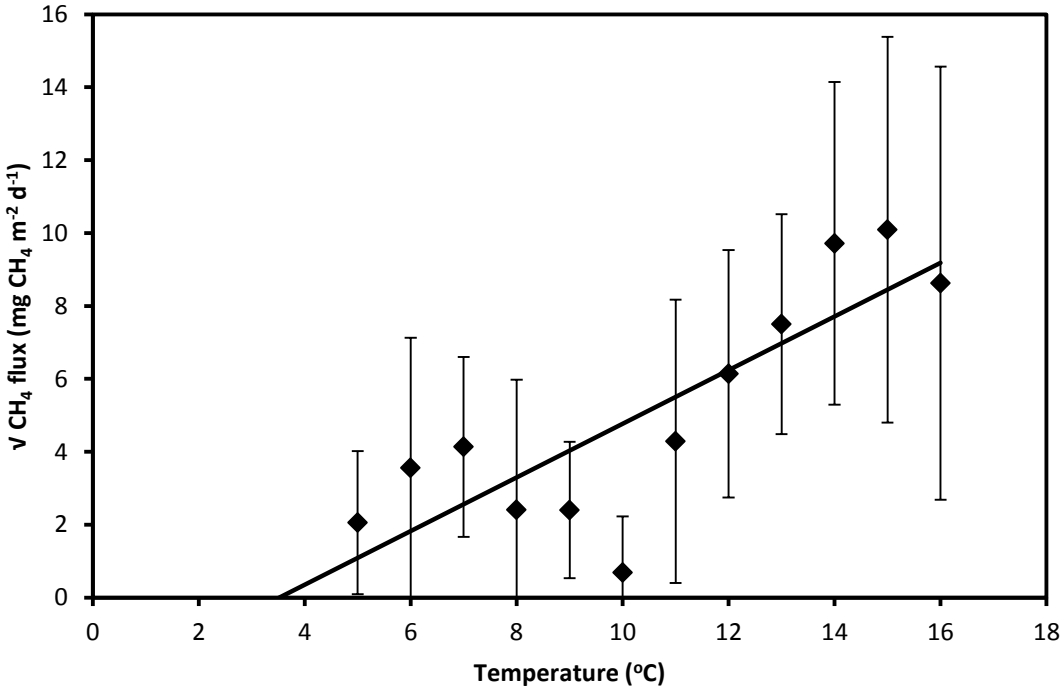

Figure 14. Relationship between soil temperature at 10 cm depth and mean CH_4 flux (square root transformation), using data from figure 13. Error bars show standard error of the mean (also square root transformation). $r^2 = 0.69$, $r<0.05$.

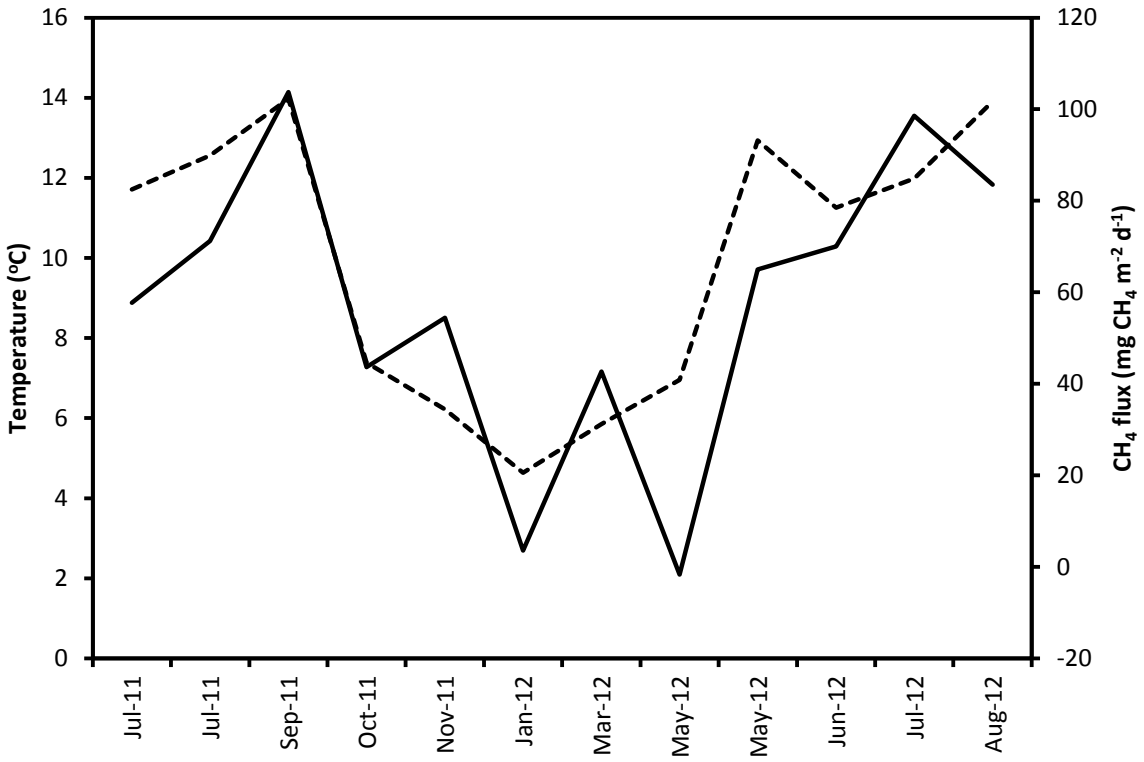

Figure 15. Mean soil temperature at 10 cm (dashed line) and CH_4 flux (solid line) for approximately one year. Data is from taken from secondary collars (including pools) and is averaged from blocked and unblocked treatments. Regression between temperature and square root transformation of CH_4 flux (as in figs. 11 and 12) gives $r^2 = 0.66$, $p<0.05$.

7.3.9. CO_2 fluxes

Tables 2 and 3 display CO_2 fluxes. Respiration (i.e. dark chamber) fluxes were largest from reprofiled ditches. NEE results suggested that bare peat within ditches was a source of CO_2, but that *Sphagnum* colonising within ditches created a CO_2 sink.

Table 2. Dark chamber (respiration) mean CO_2 summer fluxes in mg CO_2 m^{-2} hr^{-1}, plus standard error of the mean and sample number for open, dammed and reprofiled ditches. 1m and 3m refer to collars adjacent to ditches by that distance. Data is from July 2011, mid and late May 2012, and June 2012.

	Open			Dammed			Reprofiled		
	Flux	SE	*n*	Flux	SE	*n*	Flux	SE	*n*
Ditch - bare peat	67	8	12						
Ditch - *Sphagnum*	98	20	12						
Blocked ditch				135	23	15	259	73	15
1m	182	23	16	168	33	15	125	19	15
3m	132	43	12	102	10	11	108	15	12

Table 3. Net ecosystem exchange mean CO_2 summer fluxes in mg CO_2 m^{-2} hr^{-1}, plus standard error of the mean and sample number for open, dammed and reprofiled ditches. 1m and 3m refer to collars adjacent to ditches by that distance. Data is from mid and late May 2012, and June 2012. A negative sign indicates CO_2 uptake from the atmosphere.

	Open			Dammed			Reprofiled		
	Flux	SE	*n*	Flux	SE	*n*	Flux	SE	*n*
Ditch - bare peat	79	12	8						
Ditch - Sphagnum	-463	56	12						
Blocked ditch				-302	74	11	-156	150	12
1m	-196	94	12	-348	106	11	-239	90	12
3m	-326	96	12	-267	106	11	-242	122	12

7.4. Discussion

7.4.1. The effect of ditches on CH_4 fluxes

During the pre-rewetting monitoring phase, fluxes from open ditches were approximately 2.5 times larger than those from blanket bog 1 m adjacent to ditches. Fluxes from blanket bog 3 m adjacent to open ditches were midway between ditch and 1 m fluxes, but were not significantly different to either. These results suggest that ditches have the effect of drying out the bog adjacent to them, and consequently suppressing CH_4 fluxes. Additionally, the wet characteristics of the ditches appear to make them more important as emitters of CH_4. Mean flux from ditches before blocking was 11.6 mg CH_4 m^{-2} d^{-1}. Whilst higher than fluxes from the adjacent bog surface, these fluxes remain substantially lower than fluxes from ditches in agriculturally drained peatlands where fluxes of 218 mg CH_4 m^{-2} d^{-1} (Hendriks *et al.*, 2007), 623 mg CH_4 m^{-2} d^{-1} (Teh *et al.*, 2011), and 2950 CH_4 m^{-2} d^{-1} and 8780 CH_4 m^{-2} d^{-1} (Schrier-Uijl *et al.*, 2010) have been reported. It is also lower than fluxes recorded from mined peatlands in Sweden, where average fluxes from sites were 26-600 mg CH_4 m^{-2} d^{-1} (Sundh, *et al.*, 2000), and from a Finnish raised bog drained for forestry where fluxes ranged considerably, but with a maximum of 3512 mg CH_4 m^{-2} d^{-1} (Minkkinen & Laine, 2006). However, results from secondary collars did not suggest that ditches lowered fluxes from adjacent bog, as for both 1 m and 3 m collars fluxes were largest for open control ditches. Such inconsistencies demonstrate the complexity of interpreting CH4 fluxes, and are indicative of numerous controls (such as local differences in vegetation composition, water table, moisture content, and substrate availability).

Fluxes from ditches before rewetting at our study site were closer to those found by Von Arnold *et al.* (2005) who noted means of 9.6 and 9.8 mg CH_4 m^{-2} d^{-1} from ditches at two drained and afforested peatland sites. They are also similar to fluxes reported from other sites on the Migneint blanket bog, of 0.15–6.39 mg CH_4 m^{-2} d^{-1} noted by Kang & Freeman (2002) or the mean value of 13.4 mg CH_4 m^{-2} d^{-1} noted by Cooper *et al.* (2013). It seems apparent that nutrient levels and substrate availability are key factors in determining within-ditch methane emissions, as fluxes from disturbed or agricultural peatlands are consistently higher than those from nutrient-poor ombrotrophic bogs. Sundh *et al.* (2000) hypothesised that ditch fluxes were driven by within-ditch CH_4 production, rather than CH_4 being produced in anaerobic horizons in the inter-ditch areas and transported to ditches through drainage. Contrary to this, Minkkinen & Laine (2006) recorded larger fluxes from ditches with moving water, with larger fluxes from the water surface than the ditch bottom, suggestive of CH_4 transport in drainage waters from adjacent areas. Cooper *et al.* (2013) suggested that steeper ditches in blanket bogs increased ditch run off, thereby limiting the opportunity for methanogenesis to occur within the ditch itself. More research is needed to elucidate the pathway of ditch CH_4 fluxes, and to quantify the proportion of in-ditch production versus drainage inputs from elsewhere, and whether these proportions are constant or change seasonally.

Sundh *et al.* (2000) found that vegetation within ditches was involved with mediating fluxes, either through aerenchymatous CH_4 transport or by providing methanogenic substrates. They recommended that regular cleaning of ditches to impede vegetation establishment would keep fluxes low. For ditches on blanket bog this may be unnecessary as we found that fluxes from areas of within-ditch *Sphagnum* and bare peat were very similar, and both low. Roulet & Moore (1995) found that drainage had the potential to result in an increase in net CH_4 fluxes from the landscape as a whole due to the creation of ditch hotspots. Considering our results, and those of Cooper *et al.* (2013), it seems that the digging of drainage ditches on blanket bog will not have the same effect, because (as previously mentioned) our results also tentatively suggest that the digging of drainage ditches suppresses CH_4 flux from bog adjacent to ditches. Specifically, during the pre-rewetting phase of the experiment, mean fluxes from open ditches were 11.6 CH_4 m^{-2} d^{-1}, whilst fluxes 1 m from ditches were 4.3 CH_4 m^{-2} d^{-1}. It can therefore be hypothesised that drainage increases fluxes compared with those from the pre-drained peat surface, but decreases fluxes in a narrow section of bog adjacent to ditches, therefore resulting in little net change. It therefore follows

that the net effect of the digging of ditches on CH_4 flux will depend on the spacing between ditches, and the width of each ditch.

Another finding was that unblocked ditches showed negative fluxes (i.e. CH_4 consumption) on numerous occasions. For both bare peat and *Sphagnum* the incidence of this was respectively 16% and 17%. In *Sphagnum* this is explainable, as symbiotic relationships between *Sphagnum* and methanotrophs are well-documented, with methanotrophs providing a carbon source for *Sphagnum* (Raghoebarsing *et al.*, 2005, Kip *et al.*, 2010). A lack of CH_4 flux from *Sphagnum* in ditches has been observed before, and attributed to this mechanism (Minkkinen & Laine, 2006). Cooper *et al.* (2013) observed only low fluxes from bare peat, and northern agricultural peats have been observed to be net sinks of CH_4, depending on the position of the water table (Regina *et al.*, 2007). The fact that bare peat was within hydrologically active ditches might be expected to lead to large CH_4 fluxes, due to favourable moisture conditions for methanogens. However, research in northern peatlands has suggested that methanotrophy is substrate limited (Freeman *et al.*, 2002). As such, CH_4 production is stimulated in wet microsites, and CH_4 then diffuses to aerobic microsites where it is oxidised (Basiliko *et al.*, 2007). However, actual incidences of negative flux suggest that methanotrophs in bare peat have the ability to consume atmospheric methane under specific conditions. Due to the relatively small number of bare peat flux chamber measurements displaying negative fluxes, it was impossible to elucidate if these specific conditions include certain water table or temperature ranges, and therefore we cannot adequately explain this occurrence.

7.4.2. The effect of ditch blocking on CH_4 fluxes

Data from both the manual and automatic dipwells suggested that ditch blocking has, to some extent, been successful at raising water tables. This effect was clearest for reprofiled ditches, where water tables adjacent to ditches were, on average, 2 cm closer to the surface compared to unblocked control ditches. Water tables in bog adjacent to dammed ditches were 1.5 cm closer to the surface compared to unblocked control ditches, but this was only weakly significant ($p<0.1$). There was some additional evidence that ditch blocking has succeeding in raising water tables in blanket bog equidistant between blocked ditches, compared to locations where only one of the adjacent ditches has been blocked. Although these changes in water table are small, similar responses to ditch blocking have been reported. Other studies on blanket bog have noted average changes in depth to water table of 2 cm and 2.6 following ditch blocking (Wilson *et al.*, 2011, Holden *et al.*, 2011). It is

important to consider that the ditches in this study were at the very top of the catchment and therefore were relatively shallow and partly infilled in places. Ditch blocking of more incised ditches elsewhere on the Migneint has raised water tables by an average of 7 cm (Cooper *et al.*, 2013).

After taking average CH_4 fluxes for water table increments of 1 cm, a negative relationship was found between CH_4 flux and depth to water table. It would therefore be expected that ditch blocking would lead to higher water tables and associated larger emissions of CH_4. Data from gas sampling collars that were installed before ditch blocking showed large increases in CH_4 fluxes following rewetting, particularly for within-ditch collars. Caution must be exercised when drawing conclusions from these data, as pre- and post-rewetting monitoring of these collars was for different time periods: pre-blocking data were only collected from July 2010 to January 2011. Additionally, there was a significant difference in pre-rewetting fluxes between ditch collars assigned to reprofiled and dammed ditches, with mean fluxes from dammed ditches being approximately 20 mg CH_4 m^{-2} d^{-1} higher than those from reprofiled ditches. The huge increase in CH_4 fluxes from reprofiled ditches is highly suggestive of a direct effect of ditch blocking, and the pre-existing flux difference between dammed and reprofiled ditches suggests that this increase is potentially larger than a straightforward comparison of post-blocking fluxes would suggest. The high fluxes from blocked ditches are similar to those others have found: 231 mg CH_4 m^{-2} d^{-1} on blanket bog (Cooper *et al.*, 2013) and 38.6 mg CH_4 m^{-2} d^{-1} and 164.7 mg CH_4 m^{-2} d^{-1} from ditches and pools on a restored cutover bog (Strack & Zuback, 2013). Evidence for an effect of ditch blocking is also supported by the large differences in fluxes from secondary collars that were installed after rewetting: the mean flux from collars in unblocked ditches was 5.1 mg CH_4 m^{-2} d^{-1} for *Sphagnum* and 3.6 mg CH_4 m^{-2} d^{-1} for bare peat. Mean fluxes from collars in dammed and reprofiled ditches were 47.3 mg CH_4 m^{-2} d^{-1} and 116 mg CH_4 m^{-2} d^{-1} respectively, and pool fluxes in dammed and reprofiled ditches were 47.2 mg CH_4 m^{-2} d^{-1} and 186 mg CH_4 m^{-2} d^{-1}.

These data clearly show that ditch blocking leads to a large increase in CH_4 fluxes from within the blocked ditches. Bog pools have been observed to be important contributors to CH_4 emission (Waddington & Day, 2007), and our results are comparable to static chamber fluxes measured from boreal beaver ponds (Dove *et al.*, 1999). Natural pools on blanket bog have also been cited as significant contributors to landscape-scale CH_4 fluxes (Hargreaves & Fowler, 1998). The increased within-ditch fluxes following rewetting occur as water tables rise and favourable conditions for net methane production are reached

(Freeman *et al.*, 1993, Komulainen *et al.*, 1998). The two different ditch blocking techniques had different effects on within-ditch and pool fluxes; CH_4 fluxes were higher in reprofiled ditches compared to dammed ditches. Reprofiling is a more invasive technique, and involves compacting the peat at the base of the ditch to remove any hydrological functioning. Research on forestry practices on UK peat soils has shown that compacting can increase CH_4 fluxes, possibly due to the creation of favourable anaerobic conditions (Mojeremane *et al.*, 2012). Another possibility is that the disturbance to the peat, and in particular the uprooting and burial of live plant material, is providing new substrate for methanogenesis (e.g. Glatzel *et al.*, 2004).

For collars that were installed for pre- and post-rewetting phases there was no significant post-rewetting difference in CH_4 flux between blocked and unblocked ditches for collars 1 m adjacent to ditches, although there were visible (not-significant) differences in CH_4 flux, with emissions increasing in the order unblocked < dammed < reprofiled. For collars 3 m adjacent to ditches, CH_4 emissions increased in the same order unblocked < dammed < reprofiled and fluxes from the reprofiled treatment were significantly higher when compared to the unblocked treatment. However, this result is confounded by data from the secondary collars that were installed after blocking where fluxes were highest from those at 1 m and 3 m besides ditches for collars associated with open, unblocked ditches. It is therefore difficult to draw any robust conclusions about the effects of ditch blocking on CH_4 fluxes from areas between ditches. With these caveats in mind, grouping fluxes from all secondary collars suggests that mean CH_4 fluxes were highest in blanket bog with reprofiled ditches, and that fluxes from drained bog and bog rewetting through dammed ditches did not differ.

7.4.3. The effect of ditch blocking at the catchment scale

Upscaling fluxes to the landscape-scale revealed that, before rewetting, the 1.59 km^2 Afon Ddu catchment had a landscape-scale mean flux of 2.89 g CH_4 m^{-2} yr^{-1}. This is lower than calculated fluxes for two other small catchments on the Migneint blanket bog subject to ditching: 4.8 g CH_4 m^{-2} yr^{-1} at Llyn Serw and 5.6 g CH_4 m^{-2} yr^{-1} at the Nant y Brwyn (Cooper *et al.*, 2013, Cooper, 2013). However, measurements for the Afon Ddu catchment were conducted towards the top of a hillslope, on a relatively steep gradient for blanket bog, whilst the Llyn Serw site is situated in a large, shallow basin, and the Nant y Brwyn features a valley bottom with a riparian zone from which CH_4 fluxes were found to be comparatively high (Cooper, 2013). As such, the differences in landscape-scale fluxes may simply reflect the natural characteristics of each site.

After ditch blocking, the catchment budget was calculated as 3.45 g CH_4 m^{-2} yr^{-1} if all ditches were dammed, and as 4.11 g CH_4 m^{-2} yr^{-1} if all ditches were blocked using the reprofiling technique. 'Borrow pits' were then included in the calculation, which are the depressions that are left behind when peat substrate for dams is removed from the bog area between ditches. These fill with water, but also have vegetation in that was replaced after peat substrate was removed. Although no flux measurements were obtained from these areas it seems probable that they emit large amounts of CH_4 and that they may function similarly to the reprofiled ditches, as they involve disturbance to the vegetation, and the creation of shallow, vegetation-filled wet depressions. By using a mean flux value from reprofiled ditches and pools, they were factored into a post-blocking calculation. Their inclusion increased post-blocking catchment budgets to 3.55 g CH_4 m^{-2} yr^{-1} for dammed ditches and 4.21 g CH_4 m^{-2} yr^{-1} for reprofiled ditches. These figures are closer to those for undrained lowland blanket bog in Ireland where a flux of 6.2 CH_4 m^{-2} yr^{-1} was reached (Laine *et al.*, 2007), but are still higher than an earlier estimates from an undisturbed part of the Migneint were a flux of 1.1 CH_4 g m^{-2} yr^{-1} was calculated (Kang & Freeman 2002). .

As such, in the immediate aftermath of rewetting (< 20 months), ditch blocking resulted in increases in catchment-scale CH_4 flux of 23% or 46% depending on the blocking technique used. It is possible that fluxes may increase further in the near future. Peatland restoration has been observed to promote the spread of *Eriophorum* with associated increases in CH_4 fluxes (Komulainen *et al.*, 1998, Marinier *et al.*, 2004, Mahmood & Strack, 2011). Flux increases from areas of *Eriophorum* have been ascribed to the plants enhancing methanogenesis by supplying root exudates (Saarnio *et al.*, 2004, Ström *et al.*, 2012) or simply by acting as chimneys for CH_4 to bypass the aerobic zone, thus decreasing CH_4 oxidation (Greenup *et al.*, 2000, Dorodnikov *et al.*, 2011). Elsewhere in the Migneint (Llyn Serw site), two years after ditch blocking using heather bales and reprofiling, fluxes were 16 CH_4 m^{-2} yr^{-1}; three times what they were before blocking. This was attributed to *Eriophorum* colonising bare peat on the blocked ditches, and possibly an effect of heather bales supplying substrate for methanogenesis (Cooper *et al.*, 2013). This situation is not directly comparable to rewetting in the Afon Ddu catchment, where ditch gradients are steeper and revegetation seems to have occurred more rapidly. Four years after rewetting at Llyn Serw, areas of bare peat remain that have not been colonised within the infilled ditches. Nevertheless, *Eriophorum* did colonise along blocked ditches at the Afon Ddu. Primarily this colonisation occurred at the margins of pools that formed behind dams, a response that Poulin *et al.* (2011) observed following restoration of harvested peatlands. *Eriophorum* also colonised within

pools, where pool depth did not exceed 0.5 m. Although CH_4 fluxes from *Eriophorum* associated with pools and pool margins were not measured, it is likely to be high. Cooper *et al.* (2013) recorded a mean flux of 231 mg CH_4 m^{-2} d^{-1}. This is higher than fluxes we measured from pools themselves, suggesting that, even though pool fluxes are high, they are lower than those from colonising *Eriophorum*. However, measurements from pool edges dominated by *Sphagnum* and sedges from a Canadian raised bog showed a flux of 156 mg CH_4 m^{-2} d^{-1} (Bubier *et al.*, 1993); this is lower than mean fluxes from reprofiled pools, but still much higher than fluxes from dammed pools. Clearly, exact measurements from both pools and pool-associated *Eriophorum* from the same site are needed to determine which outcome is preferable for the CH_4 balance of ditch-blocked sites

7.4.4. The effect of temperature on CH_4 fluxes

An analysis of individual flux measurements and soil temperature at 10 cm returned a weak ($r^2 = 0.17$) but significant ($p<0.05$) relationship between the two variables. Although low fluxes occurred at all temperatures, there were more incidences of larger fluxes as temperature increased. Considering this, a moderately strong relationship ($r^2 = 0.69$) between the two variables was found when a mean flux value for each temperature was calculated. This suggested that fluxes started to rapidly increase as soil temperatures rose above 10^oC. Dunfield *et al.* (1993) found that CH_4 production was small below 10^oC in laboratory experiments on Canadian peats, and suggested that methogenesis is more temperature responsive than methanotrophy.

The relationship between mean CH_4 flux and mean soil temperature was also evident seasonally, with both variables being depressed during winter, and enhanced during summer. It is important to state the caveat that soil temperature was measured at 10 cm, and that several times (July 2011, May 2012) during the study the water table dropped below 10 cm. The effect of this is clear in May 2012 when the relationship between temperature and CH_4 flux diverges. It is also important to note the wide range that the temperature fluctuates over, and this can partly be considered to be due to the fact that temperature is averaged from both drained and rewetted treatments, as well as from ditches and adjacent bog. It is likely that there will be some degree of confounding here, in that other variables that control CH_4 flux will be correlated with temperature. For example, higher temperatures might be associated with an increased availability of carbon substrates (Freeman *et al.*, 2001b), and this can be dependent on the vegetation type (Inglett *et al.*, 2012). Also, an increase in vascular green area of CH_4-transporting species (VGA_{AER}) will result in increased CH_4 fluxes, and VGA_{AER}

development will be correlated with mean temperature as both variables increase into the growing season (Laine *et al.*, 2007).

7.4.5. CO_2 fluxes

Respiration (i.e. dark chamber) fluxes are comparable to those of McNamara *et al.* (2008) who recorded a mean summer respiration flux of 174 mg CO_2 m^{-2} hr^{-1} for *Calluna vulgaris* on UK blanket bog. Our results suggest that rewetting reduces fluxes from respiration for non-ditch areas, which has been observed elsewhere (Urbanovä *et* al, 2011, Tuittila *et al*, 1999). The results show a large increase in respiration fluxes from reprofiled ditches when compared to both bare peat and *Sphagnum* in unblocked ditches. Fluxes from within unblocked ditches may have been low because these ditches were hydrologically active, and therefore consistently wet. The reprofiling technique disturbs the ditch material and infills the incised ditch; it is possible that this method leads to some oxygenation of the peat within the ditch. Alternatively, this result may simply be an artefact of the small sample size (note that standard error was extremely high for reprofiled collars).

NEE fluxes are comparable to those presented by Laine *et al.* (2006) from an Irish blanket bog, but are larger, as would be expected of summer-only fluxes (i.e. mean annual fluxes are lower due to a lack of photosynthesis outside of the growing season). Bare peat within ditches was a source of CO_2 due to an absence of vegetation but within-ditch *Sphagnum* had the largest CO_2 uptake of all collars. Our survey of bog pools (refer to chapter 6) showed rapid *Sphagnum* colonisation, and therefore these results suggest that this is a favourable outcome from a carbon perspective. Considering the extremely large standard errors of the fluxes from collars 1m and 3m adjacent to ditches, and lacking a detailed analysis of the respective plant species composition of individual collars which likely drives this variation, it is difficult to draw any further conclusions of a robust nature.

7.4.6. Conclusions

Our findings show that ditch blocking increases CH_4 flux at the landscape scale, and that the magnitude of this increase depends on the blocking technique used. Reprofiling, rather than damming, resulted in the largest flux increase, possibly due to the major within-ditch disturbance associated with this technique. Bog pools in both dammed and reprofiled ditches were important emitters of CH_4. Contrary to research from more productive peatland systems, we observed that unblocked ditches were not major hotspots of CH_4 production, although they displayed fluxes that were higher than those from bog 1m adjacent to ditches.

Negative CH_4 fluxes were occasionally observed, and these were recorded most frequently in bare peat and *Sphagnum* within open ditches. This finding suggests that *Sphagnum* colonisation is desirable, within both pools and ditches, as symbiotic methanotrophs may, to some extent, ameliorate the large fluxes that are associated with these anaerobic environments. Any ditch-blocking techniques that limit the post-restoration expansion of *Eriophorum* should be encouraged, as work elsewhere on the Migneint has shown that these species are associated with large CH_4 fluxes which contribute substantially to CH_4 fluxes at the landscape scale. Additionally, post-rewetting increases in CH_4 flux from both dammed and reprofiled ditches were smaller than post-rewetting in flux increases at Llyn Serw on the Migneint, where ditches were completely filled in. Here, areas of bare peat remain, and *Eriophorum* is the only major colonising species. Considering this, a tentative policy suggestion is that damming or reprofiling methods both offer a more favourable outcome compared to completely filling in ditches, at least as far as CH_4 fluxes are concerned.

Appendix

Figure 6. Values of *n* for open, dammed and reprofiled ditches, pre- and post-rewetting.

	Ditch			1m			3m		
	Open	Dam	Re	Open	Dam	Re	Open	Dam	Re
Pre	16	16	7	16	17	13	13	16	13
Post	18	22	15	19	20	15	14	17	19

Figure 7. Values of *n* for open, dammed and reprofiled ditches post-rewetting. Sampling took place both in early and late August in 2012, hence duplication.

	2010					2011							2012			
	Jul	Aug	Sep	Oct	Nov	Jan	Mar	Apr	May	Jun	Sep	Nov	Mar	May	Aug	Aug
Open	10	5	7	9	10	7	2	3	6	4	3	4	4	7	11	7
Dam	12	6	5	8	10	8	2	4	3	4	4	3	5	8	10	6
Re	11	8	6	9	9	9	4	4	5	3	4	3	3	6	10	5

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Synthesis and Conclusions

8.1. Introduction

In Europe 52% of 'active' peatlands (i.e. ones accumulating peat naturally) have been degraded through various processes; conversion to agricultural or forested land, subjected to peat harvesting, inundated by water, or built on. Approximately 20% of European peatlands have been lost completely (i.e. they no longer exist). For the UK, it has been estimated that 8% of peatlands no longer exist (Joosten & Clarke, 2002), and much of this loss has occurred in the English fens, where 39% of deep peat is under cultivation (Natural England, 2010). When these figures are acknowledged alongside the biogeochemical changes to carbon cycling that climate change could initiate (e.g. Chapman & Thurlow, 1998, Fenner *et al.*, 2007, Pärn & Mander, 2012) there is clearly cause for alarm, as climate change could potentially create positive feedbacks, especially in peatlands already modified by drainage, agriculture or forestry, and stimulate the loss of soil organic carbon (Ise *et al.*, 2008). From a UK perspective, modelling has suggested that future climate changes will decrease the amount of area that is suitable for the continued growth of blanket bog (Clark *et al.*, 2010). Considering this, a concerted effort is now underway to restore peatland systems of various types. Ditch blocking is one such restoration (i.e. rewetting) method, and the primary focus of this PhD thesis. This synthesis will summarise the important findings under several sections: 1) methodological and analytical considerations arising from the work; 2) the effects of ditch blocking on carbon cycling and other ecosystem services, and policy implications, and; 3) ideas for future research. Throughout this chapter, mention will be made in passing to note both novel research and findings, and work that did not go according to plan or failed completely.

8.2. Methodological Considerations

8.2.1. Implications for experimental design

This PhD thesis has addressed one such rewetting project using several important approaches. Firstly, it has featured a period of baseline monitoring before ditch blocking where DOC, POC, pH, EC and CH_4 fluxes were all measured, something that has been neglected by some earlier studies (e.g. Wallage *et al.*, 2006). Evans *et al.* (2011) state in a report to the Joint Nature Conservation Committee (JNCC) that: "it is often difficult to…collect sufficient baseline measurements before the planned manipulation occurs. It is then difficult to confidently attribute observed changes in measured C fluxes to the treatment

itself, rather than to pre-existing differences between sites." The importance of this is clearly seen in the DOC data for pore water where pre-blocking differences between DOC concentrations were large: mean concentrations were 26.0 mg L^{-1} for control ditches, 41.6 mg L^{-1} for reprofiled ditches, and 31.7 mg L^{-1} for dammed ditches. These data represent large spatial variations in pore water DOC, over a small hillslope scale. Wallage *et al.* (2006) recorded median pore water DOC concentrations of 42.9 mg L^{-1} and 13.3 mg L^{-1} for a drained and blocked site respectively, which were some 1 km apart. Without pre-blocking data, there can be no certainty that their results are due to ditch blocking, and not some other, pre-existing condition.

Secondly, this study also features the use of unblocked control ditches within a wider blocked catchment. This is in contrast to some studies where all ditches within a catchment have been blocked, and control measurements are taken from a geographically distinct catchment (e.g. Worrall *et al.*, 2007, Gibson *et al.*, 2009, Wilson *et al.*, 2011a). Evans *et al.* (2011) state: "Results from any manipulation study which lacks suitable controls…cannot be unequivocally attributed to the effects of the manipulation." Although the aforementioned studies have control sites, their suitability should be rigorously examined. As the pore water DOC data presented here shows, determinands can vary extensively across a hillslope that visually looks homogenous, ergo, determinands can vary extensively between apparently similar catchments. Future studies should give strong consideration to establishing control and experimental plots within the same site. One possible problem with this design is that it could lead to confounding results. For this study, a randomised design was used with blocked and unblocked ditches mixed together, so as to minimise the influence of any underlying linear change that might be present, such as increasing peat depth. From this arises the possibility that a raised water table in a blocked ditch may influence an adjacent unblocked control ditch. Hydraulic conductivity in blanket bogs is typically low, making this unlikely, and the effects of ditches (whether blocked or unblocked) on water table are often relatively localised (Wilson 2011b, Bellamy *et al.*, 2012). Nevertheless, caution must be exercised to minimise the chances of such interactions. One option is to study ditches that flow directly down slope, rather than at an angle where water may flow more readily from blocked to unblocked ditches. The other option is to group blocked and unblocked ditches into adjacent groups thus limiting the potential for interactions between treatments, but this then introduces statistical problems involving randomisation.

Thirdly, this study possesses replication of ditches, contrary to some other studies of ditch blocking (e.g. Cooper *et al.*, 2013). This replication allows more confident inferences

to be drawn that are based on sound statistical tests. The advice of Evans *et al.* (2011) is that: "an absolute minimum of three replicates of each treatment type…is required for statistical analysis of plot-scale experiments." It can thus be seen that this study fulfils three key criteria of Evans *et al.* (2011) that are suggested as guidelines in the establishment of robust field manipulation experiments. Additionally, this study has addressed gaps in the knowledge of carbon fluxes from peatlands that Worrall *et al.* (2011) list in another report to the JNCC. Firstly, they also cite the lack of previous studies featuring both baseline monitoring and unblocked control ditches. Secondly, they point to a lack of data concerning the effects of ditch blocking on CH_4 fluxes from blanket bog. Both of these are addressed within this study. Thirdly, Worrall *et al.* (2011) point to the requirement that a better understanding of fluvial carbon fluxes is needed. This study addresses this point to the fullest extent of any ditch blocking experiment so far, by measuring water chemistry determinands in surface water (both ditches and the stream draining the experimental catchment), pore water, and overland flow. By monitoring these three hydrological components, new insights into DOC dynamics were observed suggesting that ditch water and overland flow are essentially different parts of the same flowpath. This has important ramifications for experimental studies that have solely considered DOC concentrations and water fluxes within drainage networks, which therefore omit a key part of the fluvial carbon budget.

Despite these positive findings, and in addition to the aforementioned potential for interactive effects on water table between open and blocked ditches, other problems were encountered during the study. For example, one hypothesis for a lack of treatment effect on water chemistry after ditch blocking is that the original ditches did not adequately fulfil their intended function, or that any function had been reduced by natural infilling during the intervening years. Although some sections of the experimental ditches consisted of bare peat, other sections had revegetated and infilled to various degrees (fig. 1). Ditches at the bottom of the hillslope were much more heavily incised (fig. 1), and if monitoring had taken place here it is possible that a treatment effect may have been observed. The practical reason for monitoring ditches at the top of the hillslope were two-fold: 1) to ensure that expensive equipment was distant from the road, thereby deterring would-be thieves; 2) the National Trust wanted any unblocked control ditches to be unobtrusive, as they did not believe that the general public would understand why some ditches had been left unblocked (monitoring at the bottom of the hillslope would entail a 500 m length of upstream ditch being left unblocked).

Another problem was encountered in estimating water fluxes from the experimental site. Each ditch was equipped with a v-notch weir so as to allow fluxes of DOC and POC to be calculated. Unfortunately there were extensive problems with calibrating the automatic loggers and so flow data is missing. This problem arose as robust rating curves could not be established, due to inaccurate flow gauging methods (put simply, the containers used to collect discharge were too small to accurately measure high flows). Such problems can be avoided by ensuring that all procedures and methods are properly documented and checked in advance of fieldwork.

Figure 1. Left – a naturally infilled ditch at the head of the experimental hillslope. Right – a deeply incised ditch at the bottom of the experimental hillslope.

8.2.2. Analytical considerations

Peatland restoration projects typically, but not always, involve partnerships between various organisations that may include land owners, academic institutions, and environmental protection agencies. Each separate stakeholder will often have different aims that they want to achieve through a project. Where restoration projects proceed under the guidance of land owners there can sometimes be reluctance to carry out thorough research (Evans *et al.,* 2011), and extensive disagreement can occur between stakeholders, depending on their specific area of interest (Dougill *et al.,* 2006). Such disagreements can make the funding and

implementation of useful scientific research difficult, resulting in either poorly replicated and poorly controlled studies (see previous section), or only limited money or time available for monitoring. Once finance has been procured for such projects, there is often a desire among stakeholders to start restoration as soon as possible, and this can be at the loss of a baseline monitoring period.

As such, there is considerable current interest in the use of proxies and other novel approaches to gather information in a low-cost or rapid way. For example, Gray *et al.* (2012) show that peatland CH_4 fluxes can be modelled using either plant species or plant functional groups (e.g. the presence of aerenchyma). On a similar theme, vegetation has been successfully used as a proxy for greenhouse gas emissions (Couwenberg *et al.*, 2011). Remote sensing is a popular way to build useful datasets and allow extrapolation of these proxies to a landscape scale. Although expensive, LIDAR (light detection and ranging; an airborne laser surveying technique that generates a high-resolution model of the terrain) has proved to be a valuable tool in upland research (e.g. Kincey & Challis, 2010). Indeed, a LIDAR dataset exists for the Migneint (fig. 2), and a detailed exploration of it will no doubt result in numerous practical applications, such as scaling up greenhouse gas measurements to a landscape scale, or providing information on erosion processes. With direct relevance to this project, the National Trust have been using the Migneint LIDAR dataset to prioritise future ditch blocking according to ditch depth, slope gradient and hydrological connectivity. As well as LIDAR, there are other remote-sensing techniques that are more affordable. Knoth *et al.* (2013) demonstrate the use of quadrocopters (small, rotor-powered remote-controlled machines) fitted with modified digital cameras to record near-infrared images. These images were then automatically computationally screened for vegetation type to provide information on the success of peatland restoration.

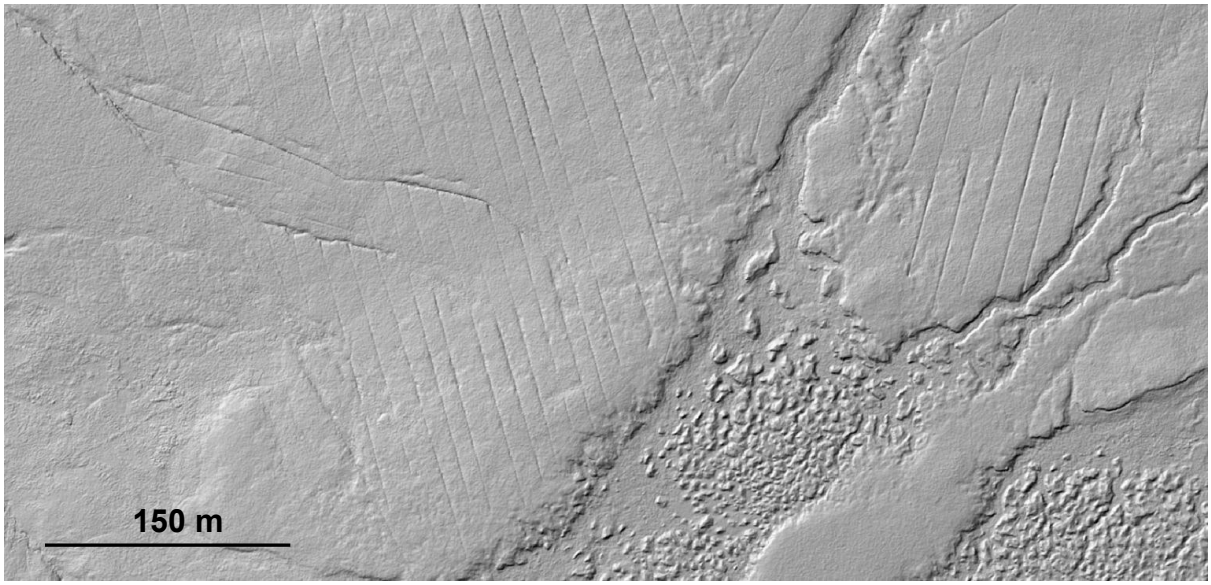

Figure 2. A small section of LIDAR data from the Migneint dataset. This shows part of the Afon Ddu experimental ditch-blocking catchment (before blocking took place). Ditches are clearly evident, as are areas of gullying (centre right). The area in the bottom and right centre that displays extensive detail is a large erosion complex.

As part of the current interest in time and cost saving measures, this project proposed a new proxy for DOC concentrations: phenolic concentrations showed considerable early promise as a proxy for DOC, comparing favourable with UV-vis proxies. Although a phenolics assay is more complicated than a UV-vis scan, it is still a relatively basic laboratory procedure. The use of a plate reader allows up to 84 samples to be analysed at once, and the essential chemicals are cheap: one litre of Folin-ciocalteau reagent costs £79.70 (Sigma Aldritch) and this is enough to run approximately 80,000 samples. One kilogram of Na_2CO_3 costs £25 (Sigma Aldritch); enough to run approximately 133,000 samples. As a spectrophotometer is much cheaper to purchase than an instrument to directly measure DOC (e.g. a total carbon analyser) then, overall, the use of a phenolics proxy offers a cheaper method. Because tests showed negligible degradation of phenolics in stored samples, water samples can be collected and stored until a sufficient number have been collected for assay. Considering this, a phenolics proxy offers an easy way to analyse a large number of samples. Where restoration projects are taking place solely under the guidance of land managers, a phenolics assay could be included in a budget and contracted out to an institution with laboratory facilities. This would allow real data on the effects of restoration on DOC concentrations to be collected cheaply, and without interfering with the other, primary aims of the stakeholder which may be more prosaic (e.g. a project to block a certain number of

ditches with the aim of improving the conservation/aesthetic value of a site, with no scientific monitoring).

Traditional thinking therefore suggests that a phenolics proxy offers an advantage over a UV-vis proxy, as absorbance is thought to decline quickly as samples degrade (Karanfil *et al.*, 2002). This would mean regular analysis of samples which, if contracted out to a laboratory, would increase staff costings. However, as part of this project weekly UV-vis scans were performed on 65 water samples for three months with no consistent change observed. This suggests that absorbance may sometimes be more resistant to degradation than previously thought, although there are caveats. For instance, samples collected from a Welsh calcareous fen showed flocculation of DOC which will affect absorbance readings (personal observations), and this has been noted previously (Römkens & Dolfing, 1998). If the absorbance of water samples from blanket bogs is consistently as stable as phenolics concentration, then a more useful DOC proxy is probably that proposed by Tipping *et al.* (2009) and further developed by Carter *et al.* (2012). This method consists of an optimised model that calculates DOC using absorbance measurements from two wavelengths. A comparison of this model against other proxies showed that the two wavelength model consistently performed well, and was the most accurate proxy for pore water DOC. The parameters cited by the model developers proved adequate to calculate ditch water DOC concentrations, and this would be expected as the model was parameterised using surface water data. As such, this provides an extremely low-cost way to estimate DOC as *no prior direct measurements of DOC concentration are required*. This is not the case for a phenolics or single wavelength proxy where a number of direct DOC measurements are needed to establish a calibration. As might be expected, the two wavelength model performed extremely poorly for pore water using the original parameters, but parameterisation against existing pore water DOC and absorbance measurements optimised it to a high degree of accuracy. A broad collaboration between those with an interest in UV-vis and DOC would be fruitful if a repository of data for different sample types could be established. This could include such variable as sample type (pore water including sampler depth, ditch water, stream water), soil type, climate (temperature, precipitation), and pollution regime. Such an approach has been suggested by Couwenberg *et al.* (2011) as a way to gap fill and provide regional calibrations. This would facilitate fine tuning of the model according to the exact characteristics of a site. Practitioners wishing to estimate DOC concentrations at a new site could then use the parameters generated from other sites that were closest in similarity to theirs.

8.3. The effect of ditch blocking

8.3.1. The effect of ditch blocking on carbon cycling

This study investigated the effects of ditch blocking on water chemistry, extracellular enzyme activities, CH_4 flux, and the vegetation colonisation of bog pools, all on the same hillslope. The results can be drawn together to provide a broad overview on the impacts of peatland rewetting. Firstly, our results suggested that mean water tables adjacent to blocked ditches had risen by 1.5 cm in dammed ditches, and 2.0 cm in reprofiled ditches (chapter 7). These slight responses are similar to other observations on UK blanket bog (e.g. Holden *et al.,* 2011, Wilson *et al.,* 2011b). Raising the water table is the primary objective of rewetting; if this objective is not reached, then widespread changes in biogeochemical dynamics can not be expected to occur. As such, the rewetting work in the Afon Ddu catchment can be considered to be a success, regardless of what other results show. It is also important to note that reprofiling appeared to raise the water table more successful than damming. No post-blocking changes were found in the activities of hydrolase enzymes or phenol oxidase (chapter 4). One explanation for this is that enzyme activities remained high as a legacy of previous conditions (Fenner & Freeman, 2011), but our data suggests that the relationship between phenol oxidase, phenolics and hydrolase enzymes is more complex than previously thought. These enzymes have been implicated in fluvial and gaseous peatland carbon cycling (Freeman *et al.,* 2001a, 2001b,), a hypothesis that our results support; we found an inverse correlation between β-glucosidase and DOC concentration, suggesting that DOC is a substrate for this hydrolase enzyme (chapter 5). Extracellular enzymes can also be used as indicators of microbial growth and activity (Frankenberger & Dick, 1983). Considering the lack of treatment effect in enzyme activity, it is perhaps not surprising that there was no sustained change in DOC concentrations or DOC quality following ditch blocking (chapter 5). This is in agreement with Armstrong *et al.,* (2010) who found no change in DOC concentration after ditch blocking, whilst others have noted only small changes (i.e. < 2 mg L^{-1}) (Gibson *et al.,* 2009, Turner *et al.,* 2013). However, there is evidence for a peak in pore water DOC concentration occurring five months after blocking, and this is followed a month later by a peak in DOC concentration in the stream draining the experimental catchment (as compared to a stream draining a nearby unrestored catchment). This transient peak is reflective of a short-term pulse of DOC, potentially due to the effect of ecosystem disturbance (e.g. Glaztel *et al.,* 2003). POC concentrations were not statistically different between open and blocked ditches due to large variations in concentration, but they were lower on average in open ditches. High POC concentrations were observed more frequently

in blocked ditches. Despite this, an enhanced concentration does not necessarily entail higher POC exports as it is possible that dams disrupt water flow down ditches and cause POC to settle out. Without water flux data it is impossible to elucidate this.

Ditch blocking was observed to increase CH_4 emissions at the catchment scale, and this increase was larger in reprofiled ditches compared to dammed ditches (chapter 7). This again potentially highlights the importance of ecosystem disturbance upon biogeochemistry; one hypothesis is that in-ditch peat compaction during reprofiling creates favourable anaerobic conditions for methanogenesis. Fluxes associated with blocked ditches were relatively stable, as opposed to fluxes associated with open ditches that displayed sudden flux changes and spikes over time. This suggests that water tables were stabilised after blocking. Bog pools that formed behind dams released large amounts of CH_4. These pools were colonised predominantly by *Sphagnum* (which preferred deeper pools) and *Eriophorum* (which preferred shallower pools) species (chapter 6). The balance of these two species and the physical characteristics of each pool will determine the strength of pool fluxes. For instance, CH_4 fluxes from within-ditch *Sphagnum* were low, and frequently negative, indicating CH_4 consumption; fluxes from *Eriophorum* after ditch blocking are large (Cooper *et al.,* 2013); fluxes of methane will be larger from smaller, shallower pools (McEnroe *et al.*, 2009). It is important to consider that this may not always be the case, however; *Eriophorum* has sometimes been associated with low CH_4 fluxes and *Sphagnum* has been associated with high CH_4 fluxes (Roura-Carol & Freeman, 1999, Dinsmore *et al.*, 2009, Wilson *et al.*, 2013). Such contrasting results demonstrate that it is important to directly measure greenhouse gas fluxes, rather than assuming that a certain vegetation composition is the preferred option to creat a carbon sink.

Upscaling CH_4 fluxes to the upper Afon Ddu catchment suggested that both ditch blocking techniques lead to increases in catchment-scale CH_4 flux, quantified as an enhancement of 23% for damming and 46% for reprofiling (chapter 7). Ditch blocking elsewhere on the Migneint has been observed to increase CH_4 fluxes by 300%, but that involved a recovery of the water table by a mean of 7 cm (Cooper *et al.,* 2013). Other studies have noted increases higher than 500 % (Komulainen *et al.,* 1998, Urbanová *et al.,* 2011). One reason for the comparatively low increase in the Afon Ddu catchment is that the measurements were conducted at the top of a slope, and therefore the bog was, relatively speaking, dry. Additionally, the figures are subject to much uncertainty, and this is partly driven by the omission of borrow pits from the sampling design. Borrow pits are shallow, flooded depressions that are created when peat is removed to build dams. Due to their

inundated environment they are likely to emit large amounts of CH_4, and as they are numerous this will be a major contribution to catchment scale fluxes. For the calculations here borrow pit fluxes were assumed to be a mean of fluxes from reprofiled pools and ditches, but, in reality, actual fluxes may be larger or smaller than this figure. In retrospect, it was an experimental oversight not to include the borrow pits, as fluxes could easily have been measured periodically using the floating chambers. Additionally, there were some contradictory results from bog adjacent to ditches, with some collars located next to open ditches displaying large fluxes and some displaying small fluxes. It is highly probable that much of this variation was due to localised vegetation differences, and an analysis of vegetation composition might have clarified this.

Finally, it is important to emphasize the fact that these results demonstrate only the short term effects (< 2 years) of ditch blocking. Any biogeochemical changes that have been initiated could take many more years before they become measurable. On such a short time scale it can be difficult to disentangle any treatment effects due to confounding seasonal variation. As the water table has been successfully raised, it would be expected that this will eventually affect the microbial communities, which will bring about associated changes to gaseous and fluvial carbon release. Likewise, the response of vegetation composition to rewetting may take several years, and the trajectory that this takes will be a major controller on greenhouse gas fluxes. Over time it might be expected that the pools created on the blocked ditch would fill in, and such a change would further alter the net flux of gasous carbon from the bog. Clearly, long term monitoring of ditch blocking projects is needed to provide information on the trajectories that rewetting may take.

8.3.2. Implications for ditch blocking projects

This experiment addressed one of four research needs listed by Lindsay (2010) in an extensive RSPB report on peat bogs: "there is a clear need for more CH_4-flux studies on UK bog systems generally…there is a particular need to investigate the CH_4 flux associated with drain blocking". Worrall *et al.* (2011) stress that carrying out restoration is the preferred ecological and conservational option for drained peatlands, and therefore recommend attempting to identify ways to mitigate increased CH_4 fluxes. This project offers some information to find a solution to this problem in three ways: 1) it compared fluxes of CH_4 from two different ditch blocking techniques and found that they differed in their effects; 2) it compared fluxes from open pools of water as well as blocked ditches, and from areas of the bog adjacent to blocked ditches; and 3) it surveyed a number of bog pools to observe how

pool characteristics influence the colonisation of plant species which are directly implicated in mediating CH_4 fluxes to the atmosphere. The effects of blocking on CH_4 fluxes from bog adjacent to ditches were found to be relatively uniform regardless of technique used, and so the net difference in CH_4 emission from a restored site depending on the type of restoration method used (assuming all are equally effective at raising the water table) will be the balance of fluxes from pools, from pool and pool margin vegetation, and from the terrestrial peat within the blocked ditches. Put simply: *all ditch blocking is not equal*. Although there is a lack of research from blanket bogs, restoration is generally seen to decrease CO_2 fluxes (Waddington *et* al, 2010, Komulainen *et* al, 1999, Tuittila *et al*, 1999), a finding that our results tentatively support. Therefore, from a greenhouse gas viewpoint and considering the CH_4 fluxes we measured, rewetting using damming without reprofiling will result in a more favourable outcome in the short term. There is a lack of information detailing the long-term vegetation trajectory after restoration, and the direction of this is important. Of concern is whether the increases in *Eriophorum* cover that is frequently observed (Lavoie *et al.,* 2005, Cooper *et al.,* 2013) is transient, or whether it is sustained. In a restored Finnish bog the cover of *Eriophorum* continued to increase over ten years following rewetting (Haapalehto *et al.,* 2011). If this is generally the case, then the combined effects of a raised water table and increased aerenchymatous plant cover will have implications for the greenhouse gas balance in the long term. It may be that direct intervention will be required to steer the species composition towards something more desirable from a greenhouse gas perspective. For example, *Sphagnum* diaspores have been manually introduced to cutover peatlands in North America with considerable success (Rochefort *et al.,* 2003), and similar management is being trialled on degraded blanket bog in the Peak District, UK (Carroll *et al.,* 2009).

Of course, the subject of gaseous carbon cycling gets more complicated when the post-restoration change in global warming potential (GWP) is examined. Although CH_4 only has an atmospheric lifetime of 12 years, compared to up to 172 years for CO_2, it is the more 'potent' of the two and over one hundred years it has a global warming potential twenty-five times that of CO_2 (Forster *et al*, 2007). As such, it is possible for an ecosystem to be a net sink of carbon, but a net source of greenhouse gases, and therefore have a positive radiative forcing effect on the atmosphere (Friborg *et al.,* 2003). Furthermore, it is possible for the greenhouse gas balance of peatlands to change temporally: a site may be a sink one year, a source the next, and neutral the year after (Herbst *et al.,* 2013). Research at present suggests that peatland restoration can lead to the creation of a greenhouse gas sink, but that this is not always the case (Höper *et al.,* 2008), and it will take longer for some sites to stabilise towards

their full potential carbon benefit (Artz *et al.,* 2012). If a favourable greenhouse gas balance (i.e. a sink, or a reduced source) can be reached than there is the possibility for ditch blocking to proceed as a mechanism to generate carbon credits, with peatlands potentially featuring prominently in future carbon markets (Dunn & Freeman, 2011). Furthermore, there is the opportunity that peatland restoration projects will be able to procure finance through the use of such markets (Bonn *et al.,* 2009). Indeed, such an approach can be considered to be a simple example of carbon sequestration by geoengineering techniques (Freeman *et al.,* 2012). Additionally, peatland drainage, restoration and rewetting is now being explicitly addressed by the Intergovernmental Panel on Climate Change, as part of a supplement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories Volume 4 (IPCC, 2013), and there is the opportunity for data from the Migneint to feed directly into this report.

The lack of a long-term response in DOC concentrations to ditch blocking will have widespread implications, as numerous restoration projects are proceeding with the involvement of water companies (Yorkshire Water, Dŵr Cymru Welsh Water, South West Water) in the hope that it offers a way to reduce DOC concentrations and therefore water treatment costs. Indeed, it is not uncommon for stakeholders to refer to DOC as a pollutant, rather than the natural component of the carbon cycle that it actually is. Whilst acknowledging that climate and management have a part to play, it has been hypothesised that the primary driver of the aforementioned widespread increases in DOC concentrations in surface waters is a recovery from acid deposition (Evans *et al.*, 2012). It is this increase in DOC concentrations that prompted the initialisation of many ditch blocking projects in the hope that they could halt or reverse the observed trend. However, if acidification is the primary driver, than these DOC increases are indicative of ecosystems returning towards natural levels, rather than destabilising due to climate or some other driver. If this is the case, then it seems almost futile to spend large sums of money on ecosystem rewetting *in the hope of improving water quality,* at least in the short term. However, drainage of blanket bogs has been observed to increase DOC leaching, and so it could still be that ditch blocking will reverse these effects in the longer term. Figure 3 displays the outcomes on the carbon balance following ditch blocking.

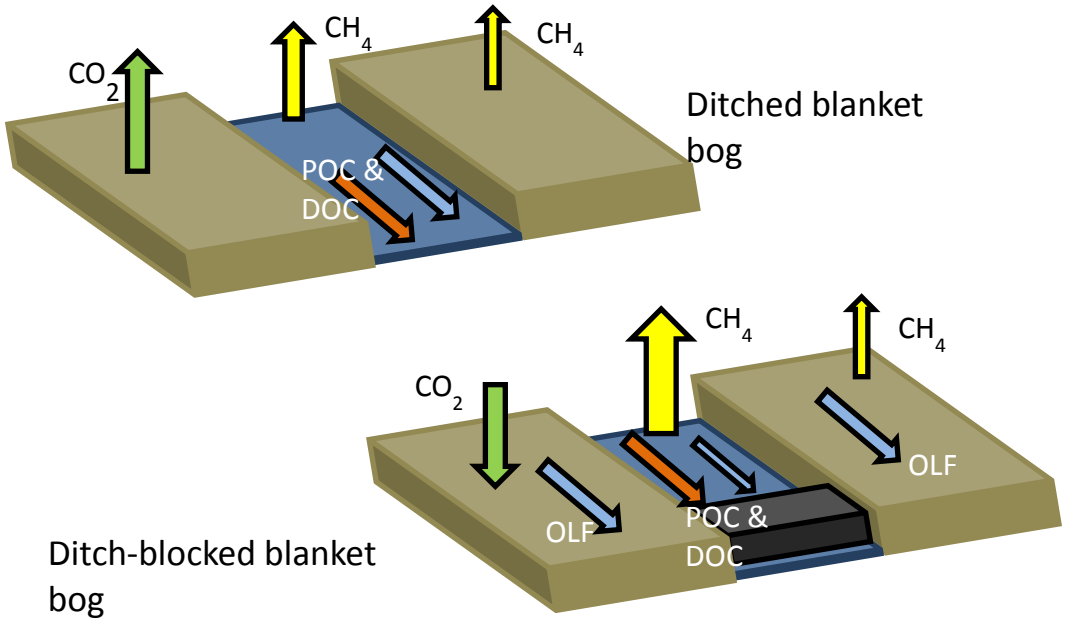

Figure 3. Conceptual diagram showing the main changes in carbon cycling following ditch blocking. Arrows indicate direction of flux. Changes in arrow size represents a relative change in flux. Ditch blocking creates a CO_2 sink and increases the CH_4 source, due to large fluxes from within blocked ditches and pools. DOC concentrations remain unchanged, but flowpaths change, with more DOC in OLF after blocking. POC concentrations remain unchanged.

8.3.3. Ditch blocking and biodiversity

Although ditch blocking was not effective at lowering DOC concentrations during the study period, it is important to consider that it did not raise concentrations, at least in the short term. Given the level of disturbance to the blanket bog associated with vehicle access, ditch reprofiling and the digging of borrow pits, this might be considered surprising, and could be viewed as a positive outcome of the study. This therefore enables restoration activities to proceed with other goals in mind. One such goal is the conservation of rare species and the maintenance of biodiversity. Although not always considered to be of high zoological importance, some endemic species are restricted to peatlands and their biodiversity is high (Warner & Asada, 2006, Renou-Wilson *et al.*, 2011). A limited number of ditch blocking studies have considered zoology with positive conclusions. Carroll *et al.* (2011) found that the wetter conditions following ditch blocking provided a more favourable environment for crane flies, and suggested that, as crane fly are a key food source for birds, restoration would therefore prove advantageous for both avian conservation and economies (i.e. grouse shooting). Ramchunder *et al.* (2012) concluded that drainage reduced the taxonomic richness of macroinvertebrates in streams, but that ditch blocking could reverse this. They hypothesised that drainage-induced increases in sediment had a deleterious effect

on stream ecosystems. Research in Ireland suggested that invertebrate taxon richness, abundance, community composition and structure were identical for pristine and restored sites. This was on a ditch-blocked site, fifteen years after restoration, where only small-scale peat harvesting had taken place (Hannigan *et al.*, 2011). It is important to consider that ditch blocking and the associated creation of bog pools will enhance the habitat heterogeneity of a peatland, with positive implications for biodiversity (Renou-Wilson *et al.*, 2011).

8.3.4. Ditch blocking and flooding

Another point of interest concerning the drainage and rewetting of peatlands is that of catchment hydrology, and the associated impact on river flows and flooding. There is a large volume of somewhat conflicting evidence on the impact of ditches on flooding, which Holden *et al.* (2004) summarise. They suggest that changes in river flows are dependent on the physical properties of both the peat (i.e. how *Sphagnum*-rich the peat is, its hydraulic conductivity) and the drainage network (i.e. ditch depth, ditch spacing, density of ditches), and that therefore drainage can increase downstream flooding in some instances. As such, ditch blocking is frequently cited as having the capacity to reduce downstream flooding. This is the case for ditch blocking on the Migneint (BBC, 2011), although the experimental design was never designed to test this hypothesis. This can partly be assumed to be an attempt to increase local support for restoration projects as the Afon Conwy that drains the Migneint is prone to flooding (Oliver *et al.*, 2008), and there was considerable local objection to the rewetting work when it was first mooted (BBC, 2007). During 2012 there was a perception within Ysbyty Ifan (a village 7 km down the Afon Conwy from the Migneint) that ditch blocking had lowered high flows on the river (National Trust, personal communication), but this could easily be explained as a placebo effect; i.e. local media and the National Trust had claimed that flooding would be reduced, and therefore locals only notice signs that fit within this hypothesis. At present there is a lack of robust evidence testing the response of river flows to ditch blocking. The only relevant study so far is that of Wilson *et al.* (2011b), who recorded a decline in the magnitude and occurrence of peak flows within ditches and small upland streams on a Welsh blanket bog after rewetting.

8.3.5. Ditch blocking and aesthetics

It can be argued that ditch blocking has an aesthetic benefit. Although much of the UK upland environment is the result of anthropogenic activity (e.g. livestock grazing, heather burning) (Holden *et al.*, 2007), this is often overlooked, and moorlands are appreciated for

their scenery and perceived wildness (Davies, 2006). Ditches are a more intrusive sign of anthropogenic activity, and it follows that the blocking of them results in a more aesthetically pleasing environment (Bonn *et al.*, 2009). In support of this hypothesis, results from our study site showed that vegetation rapidly colonised pools behind dams, and modelling has suggested that rewetting can lead to positive increases in plant species biodiversity (Bonn *et al.*, 2009). As more plant species colonise the ditches and dams, their lines will become less obvious and the former ditches will become less visually obvious.

8.3.6. Practical applications

Considering the results of this thesis, direct practical advice for rewetting can be described. The primary aim of ditch blocking is to raise the water table, and so a reprofiling method is preferred over a damming method, although this will lead to larger CH_4 fluxes compared to a damming approach. The creation of bog pools as a side effect of ditch blocking should be welcomed in part, as it will enhance the habitat heterogeneity and biodiversity of the bog. Pool characteristics should not affect DOC concentrations, but will control CH_4 and CO_2 fluxes. It may be possible to mediate these fluxes through the creation of deeper pools which are sometimes associated with lower fluxes.

Monitoring of water chemistry (DOC, pH, EC, sulphate) should take place at both a small scale (i.e. individual ditches) and a catchment scale (i.e. stream draining a bog), as any changes in biogeochemistry may not be seen at both scales. Water chemistry should be monitored as frequently as is feasible, ideally at monthly intervals. If direct DOC measurement is not possible then we recommend the use of a phenolic or UV-vis proxy, and this should provide accurate results even with a small number (< 25) of DOC calibration measurements. Measurement of CH_4 and CO_2 fluxes should also take place on a monthly basis. As static chamber sampling is time consuming the dominant vegetation types and microforms should be targeted where changes will be largest (i.e. blocked ditches, bog pools). Enzyme analyses (or other, more direct measurements of microbial activity) should be welcomed but, due to the complex interpretations of such results, are not essential.

Finally, we again stress the need for pre-treatment baseline data, and for unblocked controls alongside the rewetted treatment. Such an approach is the only sure way to eliminate differences between control and treatments sites that results from geographically distinct sites.

8.3.7. Summary

After examining all the evidence, it seems that the benefits of ditch blocking are more numerous than the negative effects (summarised in table 3). However, from an ecosystem services perspective, it should be noted that these variables are not perceived to be of equal value. For example, a group of stakeholders for the Migneint concluded during a consultation exercise that biodiversity is the most important ecosystem service, followed by carbon storage, freshwater provision, and landscape (Bonn *et al.*, 2009). There is a danger in taking this approach, in that each interested party will prefer restoration tailored towards maximising benefits from different ecosystem services depending on their knowledge and area of expertise, i.e. the tourist industry may favour a 'naturalised'/rewilded landscape as it attracts visitors and thus generates their revenue; water companies will favour restoration techniques believed to lower DOC concentrations and fluxes, etc. Although these viewpoints may not be mutually exclusive they highlight the need for extensive consultation of stakeholders before the detailed plans of restoration projects (i.e. method of ditch blocking, how many ditches are blocked) are carried out.

Table 3. A summary of the expected changes following ditch blocking. – indicates a negative change, + indicates a positive change, ≈ indicates no change, and ? indicates an unknown change. Note that these are negative or positive changes for each ecosystem service, not negative or positive changes in flux/concentration.

Variable	Change
CH_4 flux	–
CO_2 flux	+
GWP	+
DOC	≈
POC	≈
Biodiversity	+
Flooding	?
Aesthetics	+

8.4. Knowledge gaps and future research

Although this study has addressed numerous questions, many more remain unanswered. This section will summarise some of these.

1) What is the relationship between pool depth, area and CH_4 flux? The exact balance of fluxes from pools, pool vegetation, and pool margin vegetation needs to be quantified. This would enable ditch blocking projects to aim for a pool assemblage that

minimises greenhouse gas fluxes. As well as this, flux measurements from flooded borrow pits are urgently needed as they are likely to be important hotspots of CH_4.

2) Although this study gave data on DOC and POC concentrations, data on fluxes are still generally lacking. Considering the large water fluxes and low rates of evapotranspiration in the cool, high-rainfall environments in which blanket bogs occur, DOC fluxes are unlikely to decrease substantially without an associated decrease in concentration. On the other hand, it is entirely plausible that POC fluxes will decrease as dams disrupt ditch water flow and cause sediment to settle out. It seems likely that the best approach to answer this question will be that of BACI (before-after-control-impact); measuring concentrations and fluxes from streams draining pristine, ditched, and ditch blocked catchments.

3) What are the differences in transient and long-term responses, particularly for water chemistry determinands? It might be that DOC concentrations eventually start to decrease in response to the new hydrological regime stabilising and leading to steady changes in vegetation cover, microbial assemblages, and other factors that influence DOC. To begin to address this question, at least two more years of water chemistry data will be collected from the study site.

4) This study found a lack of water chemistry data for overland flow, and this knowledge gap was not restricted to blanket bogs but was universally noted. DOC in OLF may turn out to be dependent on a wide range of factors: the climate, the presence of ditches (and of borrow pits), the vegetation species present, the gradient of the site, and numerous other variables.

5) What is the effect of ditch blocking on the full carbon budget of a site? CO_2 flux measurements are needed to answer this question, and N_2O fluxes may be necessary athough measurements taken during this study, and those from the literature, suggest that N_2O will be negligible from blanket bog. A full budget also requires measurements of dissolved gases within ditches and streams, methane ebullition, and transport of dissolved gases and DOC through natural peat pipes. As other research has shown that the radiative forcing of a site can vary temporally, consecutive years of monitoring are needed to ensure no erroneous conclusions are reached.

6) Considering that flood regulation is frequently cited as a reason to block ditches, there is a lack of information concerning stream flows and incidences of flooding after restoration. It could be difficult to gather direct evidence for this, because flooding typically occurs far downstream, and peatlands often occupy the headwaters of rivers. There are therefore many other land management and climatic factors in operation that can create high

or low flows, making it problematic to elucidate the effect of ditch blocking in a small, remote catchment area.

8.5. Final word

Peatland ditch blocking is still in its relative infancy. Whilst it is becoming clear that it cannot fulfil some of its early promise (i.e. greatly decreased DOC concentrations) other lines of inquiry look to be worth pursuing, particularly positive changes in biodiversity and carbon sequestration. Most of the published work to date has reported data on short term projects (i.e. only a few years after ditch blocking) and in part this is to be expected, as research funding is normally limited. Any studies on older ditch blocked sites have therefore lacked pre-restoration data. It is essential that new projects attempt to gain funding for longer monitoring periods, or that money is made available to maintain existing projects, even if this is at the cost of reduced frequency or range of measurements. The history of UK moorland is one of changing management with changing needs, and restoration appears to be the next chapter in this story. Whereas past management has been typified by exploitation, it can be hoped that the current wave of restoration activity marks the beginning of a more sustainable relationship with our upland environments.

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