Source and Management of Water Colour in the River Tees Is the blocking of peat drains an effective means of reducing water colour from upland peats at catchment scales?

TURNER, EMILY,KATE

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Source and Management of Water Colour in the River Tees

Is the blocking of peat drains an effective means of reducing water colour from upland peats at catchment scales?

Emily Kate Turner

Department of Earth Sciences

University of Durham

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Abstract

Source and management of water colour in the River Tees. Is the blocking of peat drains an effective means of reducing water colour from upland peats at catchment scales?

Emily Kate Turner, Department of Earth Sciences, University of Durham

Extensive drainage of UK peatlands has been associated with dehydration of the peat, an increase in water colour and a loss of carbon storage. Water colour has been found to be proportional to the concentration of fluvial dissolved organic carbon (DOC) (McKnight et al. 1985). It has been considered that the blocking of drainage channels represents a means of peat restoration and a way of reducing DOC losses to surface waters. This study aimed to assess the effectiveness of drain blocking at both an individual drain scale and at a larger catchment scale (up to 1km^2). The effect of external parameters become more pronounced as the DOC record is examined at larger scales. The catchment is an open system and water chemistry will be influenced by mixing with water from other sources. Also it is likely that at some point the drains will cut across slope leading to the flow of any highly coloured water down slope, bypassing the blockages, and entering the surface waters downstream. Degradation of DOC will occur naturally downstream due to the effects of light and microbial activity. There is, consequently, a need to examine the wider effects of drain blocking at a catchment scale to ensure that what is observed for one drain transfers to the whole catchment.

A series of blocked and unblocked catchments were studied in Upper Teesdale, Northern England. A detailed sampling programme of stream water, soil water and run off was undertaken in which a series of drains were studied in the 12 months prior to and post blocking. Water table depth, flow and weather parameters were also monitored.

This study could not find a significant decline in DOC concentration at zero or first order scale post blocking; however a small yet significant decline of 2.5% in DOC concentration relative to the control catchment was recorded at the first order scale. A decrease in DOC concentration is recorded as water flows from the zero to the first order in the same catchment. The study found that the effects of DOC degradation in the catchments were very small and that DOC degradation could not solely explain the decrease in DOC concentration seen from zero to first order drains indicating the importance of dilution effects in the catchments. The blocking of peat drains does significantly decrease the export of DOC which is largely achieved by decreasing water yield. The size of the DOC export reduction caused by drain blocking is seen to decrease as scale increases providing evidence for the existence of bypass flow around the zero order drain blockages. Blocking was found to have little impact on the level of the catchment water table. This can be explained by the peat bog being naturally very wet before intervention such that when blocking did occur the soil had little capacity to take in additional water. Water yield, however, is seen to decrease post blocking indicating that water and potentially DOC is being lost from the system. Principle component analysis and event analysis were performed on the hydrological and chemical data in order to trace and define this missing component of the water balance yet the analysis found that the water chemistry in the study catchment can be defined by a relatively simple mixing trend. As such this missing water remains undefined. The presence of bypass flow and water mixing will reduce the efficiency of any drain blocking and have wider implications for upland management and its practitioners.

Declaration and Copyright

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

Signed

Date

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This hydrological monitoring study forms part of the Tees Water Colour Project (TWCP). A project spearheaded by Northumbrian Water Ltd that "*aims to link water treatment with upland management by developing, demonstrating and promoting a more holistic approach, to try to address deteriorating water quality at source, in the upstream catchment and to promote the potential additional benefits of such an approach to the wider environment and to other stakeholders*"
(Northumbrian Water Ltd, 2010, www.nwl.co.uk/Teeswatercolourproject.aspx)

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1. Introduction

1.1 Introduction

The removal of water colour from rivers draining peat covered catchments in Northern England is a major problem for water treatment works (Gibson, 2006). Attempts have been made to reduce the increasing levels of water colour by employing catchment management strategies at the water source. This project considers the success of blocking open drainage channels (commonly known as grips) as a means of reducing water colour, largely dissolved organic carbon, (DOC) at catchment scales.

This chapter aims to introduce the problem under discussion. It will explain the scientific rationale behind the project before reviewing previous studies. It also aims to outline the differences between this study and others and explain the need for a study of this nature.

1.2 Project Rationale

1.2.1 The water colour trend

The Broken Scar Water Treatment Works in Darlington, Northern England, is run by Northumbrian Water Ltd and provides fresh water to approximately 100,000 people across Darlington and the surrounding area. On a daily basis it supplies approximately 150 million litres of water to households and businesses. The majority of water originates in the Upper Tees catchment where the land is privately owned and managed. Much of the catchment is blanket bog with heather and grass moorland. This includes 29 000 hectares of designated Sites of Special Scientific Interest (SSSI).

Long term records exist for the observed fluvial dissolved organic carbon (DOC) concentrations, as water colour, at Broken Scar (Fig. 1.1, Worrall et al., 2003). This dataset indicates an approximate doubling in average water colour levels over 30 years. Since colour is generally proportional to the concentration of DOC (McKnight et al., 1985) this implies a similar increase in the concentration of DOC in the river water at the treatment works.

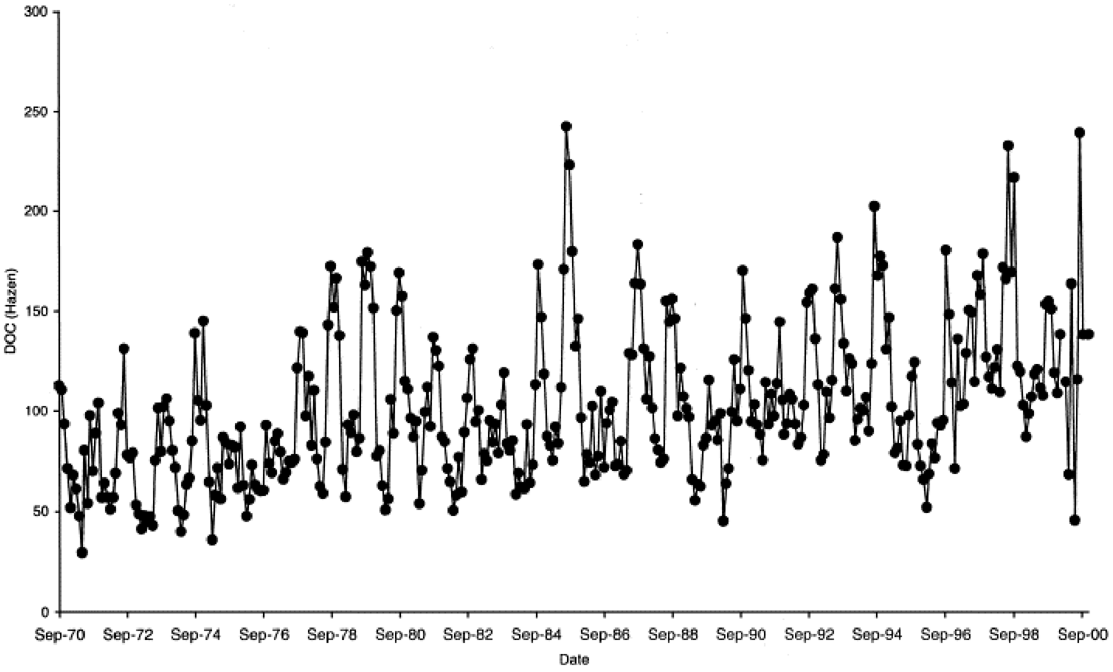


FIG 1.1: The DOC concentration trend for the Broken Scar Water Treatment Works (Worrall et al., 2003).

This trend is not confined to the Broken Scar catchment. Freeman et al. (2001a) showed that for a series of UK streams over a period of 12 years an increase of 65% in DOC flux can be seen. A study by Worrall and Burt (2007b) of 315 UK catchments found that 68% showed a significant increase in DOC concentration, 18% showed no change. However increases are not universally observed. Worrall and Burt (2007b) found that 14% of the studied catchments showed a significant decline in DOC concentration. These observed declines were largely confined to the south west corner of England. Similar decreasing DOC concentration trends have been observed in Norway (Skjelkvale et al., 2001). Monteith et al. (2007) conducted a study of 522 remote lakes and streams across North America and Northern Europe examining the DOC concentration trend from 1990 to 2004. 88% of the trends that were found to be significant were positive and most frequently found in the Southern Nordic area, the UK and North Eastern USA. Declining DOC concentration trends were found in Atlantic Canada which was attributed to increased sea salt deposits.

Over half (55%) of the UK population receive their domestic water supply from a peat covered catchment (Worrall et al., 2004). The current EU drinking water standard for water colour is 20 Hazen, the level at which there is no visible sign of colour (EU Directives 80/778/EEC, 2008). The incomplete removal of DOC during water treatment not only produces water of a low aesthetic quality but also can increase the risk of biological contamination from other sources. During water treatment chlorine is added to help limit contamination. There is a tendency for DOC to absorb chlorine, thus compromising this process meaning that there is a greater threat from other potential pollutants (Singer, 1999). The presence of DOC can also lead to the formation of carcinogenic tri-halomethanes (mainly chloroform, $CHCl_{3,}$ but also brominated tri-halomethanes where bromide is present) the concentration of which is limited by law in UK drinking water (Hsu et al., 2001) because of suggested links between the ingestion of tri-halomethanes and bladder and rectal cancer (Morris et al., 1992). Furthermore, as DOC concentrations increase more flocculation sludge is also produced from its removal and many water treatment works are designed with a limit on the level of sludge removal they can safely maintain: if DOC levels exceed this level the water treatment works may fail.

1.2.2 Implications for Carbon Storage

Catchments with extensive peat coverage commonly have high fluvial DOC concentrations (Dawson et al., 2002) (Fig. 1.2). Holden et al. (2006) states that "*these areas are recognised as a globally important component of terrestrial carbon storage as they contain a high proportion of partially decomposed organic matter of which approximately 50% is organic carbon*". Peatlands cover only 3% of the Earth's land surface but boreal and subarctic peatlands store about 15-30% of the World's soil carbon as peat (Limpens et al., 2008). UK peatlands store more carbon than the forests of Britain and France combined (Worrall et al., 2007b). The transport of DOC to the marine environment via rivers is a significant part of the global carbon cycle. The export of DOC dominates the total carbon flux in many peatland streams. Dawson et al. (2002) and Hope et al. (1994) estimate the global riverine flux to be between 1 and 10^{11}kg C yr^{-1}. The significance of maintaining peatland carbon stores is important in attempts to combat climate change which itself is driven by the release of greenhouse gases. Peat bogs are currently considered a net sink of carbon; however the increase in carbon loss suggests a shift in trend from sink to source with important implications for the carbon cycle. Worrall et al. (2009) considered a catchment of 11.4km^2 in Northern England for a period of 13 years. The study showed that over the 13 year period the total carbon balance varied between a net sink of − 20 to − 91 Mg C/km^2/yr. Extrapolating the general findings of the carbon budget across all UK peatlands, Worrall indicated an approximate carbon balance of − 1.2 Tg C/yr (± 0.4 Pg C/yr).

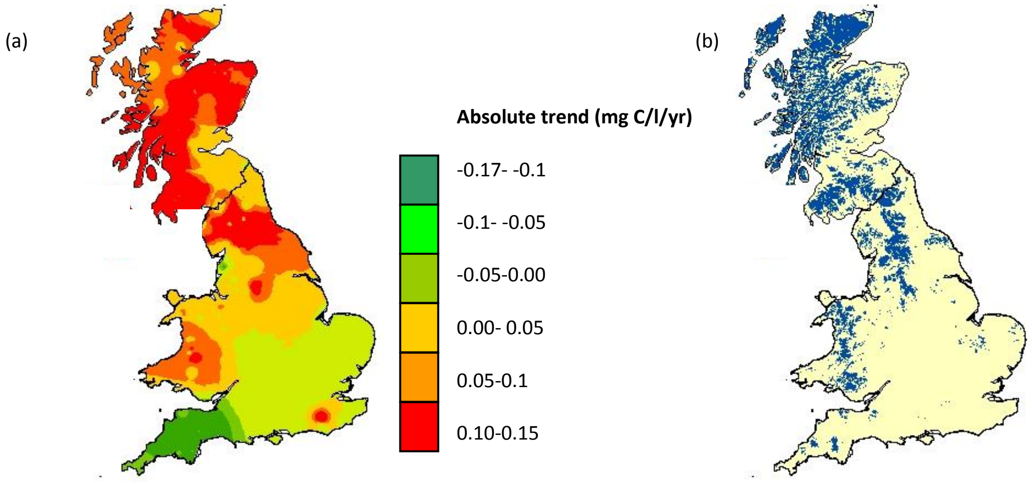


FIG.1.2: (a) The DOC loss trend in the UK (Worrall and Burt, 2008). (b) The distribution of peat soils (Milne and Brown, 1997).

1.2.3 Options for DOC removal

The standard treatment for DOC removal is at the point of abstraction i.e. at the water treatment works. Water entering a treatment works undergoes a series of treatment processes; pre-treatment to remove larger debris which may damage equipment, followed by coagulation, settlement, filtration and disinfection. Organic compounds causing water colour are usually removed via coagulation and flocculation with the removal of floc through a combination of sedimentation in settling tanks and filtration. Coagulation is commonly achieved through the addition of iron sulphate compounds or alum (hydrated potassium aluminium sulphate). Negatively charged volatile particles are attracted to the positively charged coagulant which then falls from suspension due to the increase in weight (Adger et al., 2004). Any DOC remaining in the water at the filtration stage of treatment can lead to the clogging of microfilters and blocking of adsorption sites in granular activated carbon (GAC) filters (Fearing et al., 2004).

The efficiency of coagulation and flocculation as a DOC removal method is limited by the capacity of the mixing and settling tanks; and due to the holding time required for the process, by the demand for fresh water. Furthermore, water colour represents the major recurrent cost in water treatment. At one treatment works the cost of DOC removal is £360 000 per year at present values. Newer approaches to DOC removal are being developed such as the use of the proprietary magnetic ion exchange (MIEX) resins. The MIEX resin is an anion exchange resin, used in the form of small beads, which has a magnetic component along with a macroporous structure and a high ion exchange capability to lead to higher DOC adsorption. This process greatly improves and speeds up the coagulation of the resin beads when the stirring process stops and allows for greater recovery of the loaded resin (Bursil, 2001). Greater resin recovery reduces costs both in terms of the amount of resin required and because filters do not become clogged so rapidly. However, despite MIEX resin processes potentially extending the levels to which water colour can be successfully treated, the increasing DOC trend still suggests that colour removal will become an ever greater part of treatment costs.

Water companies, particularly those treating water from peat catchments where high colour loads are to be expected are therefore seeking alternatives to “end-of-pipe” approaches to colour removal by investigating methods that would reduce the levels of DOC production at source.

1.2.4 Causes of increased colour production

Peat soils have been shown to be a major source of DOC to the drainage network. Urban et al. (1989) and Aitkenhead et al. (1999) linked the presence of extensive peat cover in a catchment to high riverine DOC concentration. The production of dissolved organic matter in peat soil was described by McKnight et al. (1985) as a microbially-driven oxidation process i.e. a process of organic matter decomposition. McDonald et al. (1991) continued by describing water colour production in peat soils as a two stage process: aerobic conditions enabling greater bacterial decomposition, followed by increased wash-out upon rewetting. This link to aerobic conditions was demonstrated for DOC by Tipping et al. (1999) who linked increased DOC production to drying of the soil.

The cause of the increasing DOC trend remains unclear but recently proposed hypotheses reviewed by Evans et al. (2005) include: historic summer drought (Worrall et al., 2004), increasing air temperature (Freeman et al., 2001b), changes in land management (Yallop and Clutterbuck, 2009), increasing atmospheric CO_2 (Freeman et al., 2004), change in flow patterns (Tranvik and Jansson, 2002), decrease in acidic deposition (Evans et al., 2006) and eutrophication (Worrall et al., 2007).

One possible reason for the increase in the DOC trend is a general decrease in mineral acidity following decreases in acid rain deposition. Krug and Frink (1983) linked this to increased DOC production. Grieve (1990) showed that when lime was applied to catchments (causing increased pH) DOC concentration in the stream network was seen to increase. Evans et al. (2006) suggested that decreasing mineral acid deposition particularly decreases in sulphur deposition, together with increases in temperature, were most likely drivers for increasing DOC trends in the UK.

A second possible reason for the increase in DOC concentration is through changes in hydrology, particularly through changing patterns of rainfall. Burt et al. (1998) note a trend in UK rainfall patterns towards wetter winters and drier summers and Osburn and Hulne (2002) found that the wetter winters were particularly manifested by an increase in heavy rainfall events. In the context of a relationship between water table drawdown or drought periods and increased DOC export (discussed below) the drier summers may lead to increased DOC export in the autumn rewetting period (Scott et al., 1998). However, the relationship between DOC concentration and DOC export, which is also dependent on changes in flow patterns, is less clear. Forsberg (1992) found that increased precipitation was responsible for the majority of increases in DOC export into several Swedish lakes but Tranvik and Jansson (2002) show that changes in the annual cycle of precipitation may be more important. Tranvik and Jansson (2002) showed that decreasing precipitation may decrease overall DOC export, as decreasing discharge leads to longer retention times in lakes, allowing greater DOC removal but equally that decreased discharge will cause increased DOC concentration in the soil runoff. Therefore, although decreasing precipitation may lead to decreased DOC export from a catchment, this will depend on the scale of the system and effect on the overall hydrology of the system.

A third possible reason for the increases is through increases in temperature. Freeman et al. (2001a) connected the increases in DOC that they observed with rising atmospheric and peat temperature, due to increases in the activity of the phenol oxidase enzymes at higher temperatures. Freeman et al. (2004) demonstrated that phenol oxidase has a key role in increasing DOC production as the phenolic compounds it removes are themselves responsible for inhibiting the activity of hydrolase enzymes involved in decomposition. Worrall et al. (2003a) also observed a correlation with temperature and linked this to an increase in microbial decomposition of peat. Tipping et al. (1999) demonstrated this directly by transporting peat cores to warmer, drier locations and observing a subsequent increase in the production of dissolved organic matter relative to control sites. Furthermore, temperature may play a role through increased faunal activity, particularly that of enchytraeid worms, the activity of which is strongly related to DOC concentration (Cole et al., 2002).

Analyses of long term records of DOC export show clear positive correlation between periods of water table drawdown and subsequent increased export (e.g. Naden and McDonald, 1989). Freeman et al. (2001b) proposed the theory of an “enzyme latch” mechanism by which the colour production is understood not simply as an aerobic process, but rather as one where hydrolase enzymes responsible for decomposition and DOC production are inhibited by the presence of phenolic compounds. These build up under anaerobic conditions because the activity of the phenol oxidase enzyme is inhibited in the absence of oxygen. Given a period of water table drawdown, leading to previously anaerobic conditions becoming temporarily aerobic, the action of phenol oxidase is increased and these repressive phenolic compounds are removed. Activity of hydrolase enzymes can then increase (Freeman et al., 2004) enabling greater DOC production which can continue even following water table restoration and the return of anaerobic conditions. The theory implies that water table fluctuations can potentially have a large effect on DOC export, which may extend for several years after restoration of the water table. Large water table fluctuations would occur at times of severe drought and so large increases in DOC concentration and or export could be expected after times of drought. Clark et al. (2005) considers an alternative drought mechanism to the enzyme-latch. Clark et al. (2005) found that in drought years DOC concentrations were suppressed in response to increased H^+ ions and increased ionic strength associated with the oxidation of inorganic/ organic S to SO_4. Low concentrations of DOC during drought years have been recorded in streams at many other sites. The reason for this has often been attributed to peat hydrophobicity causing a lagged response of 3-4 years in DOC release (e.g. Watts et al., 2001), low runoff volumes during drought years (Pastor et al., 2003) or mineralization in favour of CO_2 (Freeman et al., 2004). However Clark et al. (2005) found that the temporary acidification of the peat soil solution during drought suppressed DOC release without showing significant changes in stream water pH. Furthermore, slow rates of SO_4 reduction following rewetting could introduce a lag of several months between DOC production and response in soil and stream water. Birch (1958, 1960) considered wetting and drying sequences in organic rich soils. It was found that this led to an increase in both carbon and nitrogen mineralisation thus increased carbon turnover.

Worrall et al. (2008) reviews several lines of evidence to support the proposal that severe drought enhances DOC production and thus controls the observed increases in DOC concentration. Worrall et al. (2003) observed step changes in the DOC flux record after severe drought and Worrall and Burt (2004) demonstrated a change in the relationship between flow and DOC after a severe drought that can persist even through more minor droughts. Furthermore, soil respiration and DOC production were observed to become decoupled after a severe drought implying a change in DOC production mechanism (Worrall et al., 2005a). Finally, drought frequency and/or severity in northern peatlands is known to have increased over the period for which DOC increases have been observed (Worrall et al., 2006b). Worrall et al. (2008), however, found no clear evidence for a widespread drought effect with severe drought occurring across regions which demonstrate different DOC responses and no common pattern of DOC increase could be observed after two severe droughts. Although correlations could be found between the water flux changes and DOC flux changes, these changes after drought were dominantly controlled by changes in hydrological throughput.

Spatial variations in land management practices in UK uplands may provide potential localised drivers of environmental change over and above those that may be occurring at a larger scale (Yallop et al., 2009). Other than drainage (discussed in section 1.3) UK upland peat areas are subject to livestock grazing and controlled burning as a means of increasing production of red grouse (*Lagopus Iagopus* L.) in order to improve game shooting. To date there is little evidence to suggest that grazing has any direct effect on DOC although the consequences of burn management have been studied. Under well-managed rotational burns interstitial DOC concentrations may be lower (Worrall et al., 2007) although accelerated surface erosion, increased infiltration and throughflow (Imeson, 1971), more extreme and variable temperatures (Fullen, 1983), increased porosity (Mallik and Fitzpatrick, 1996) and reduced carbon sequestration (Garnett et al., 2000) have all been found on moorland under burning management. Although not quantified, Mitchell and McDonald (1992) noted higher colour in surface waters from catchments with extensive burning and Yallop et al. (2008) found a highly significant relationship between the extent of burn management on blanket peat and water colour in drainage waters.

In summary several hypotheses have been put forward to explain the increases observed in the DOC record, but none as yet have been universally accepted. Clark et al. (2010) states that "*research in this area appears to have reached a stalemate between those favouring declining atmospheric deposition, climate change or land management as the key driver of long-term DOC trends*". This study considers the effects of land management where it is believed that carbon release from upland peat can on the whole be related to changes in water table depth in the soil profile. An increase in the depth to the water table by peatland drainage increases the area of oxidation in the soil and it is within this oxidised area that DOC is produced. It is therefore proposed that land management strategies such as peatland drainage, or gripping as it known locally, which result in a lowering of the water table in peatlands may be implicated in the increased colour production and runoff.

1.3 Background to peatland drainage

1.3.1 Peatland management

For decades upland peat moors in the UK have been managed as a major part of the rural economy. Key goals as with any land-based economy have been to maximise the economic potential of the land. Blanket peatland is largely unsuitable for cropping and so the main farming in these areas has traditionally been sheep grazing. In addition, the habitat is also that of grouse and other game birds which has led to the development of large estates where the main economic use of the area is for shooting and sport.

The use of UK uplands for these purposes has led to a system whereby many areas of peatlands are actively managed to maintain the habitat in the optimum condition for the grouse and sheep both of which have specific requirements such as sufficient new, edible shoots of heather (*Calluna vulgaris*) and areas which are not entirely waterlogged. Techniques for this have been developed and refined over time. These techniques include the varying of grazing patterns and areas in which grouse are bred and shot in any particular year; the burning of areas of heather on a suitable timescale to encourage sufficient regrowth without damaging the underlying ecology; and in recent decades modifying the natural drainage of the peatlands by use of artificial drains.

1.3.2 Rationale for and problems with drainage

One of the perceived problems in peatland management has been insufficient drainage in many areas, especially large, relatively flat areas of blanket peat. The hydraulic conductivity of blanket peat can vary greatly (Rycroft et al., 1975) and is much higher in the topmost, aerobic layer than in the underlying permanently saturated layers. This gives rise to a two layered or “diplotelmic” model of peat behaviour with the layers being known respectively as the acrotelm and catotelm (Ingram, 1978). The acrotelm is the region within which the water table fluctuates and along with higher hydraulic conductivity has a greater density of microorganisms and living plant material (Holden and Burt, 2003a). In flatter areas where lateral drainage is slower due to the lack of slope, the water table can often be at or extremely near to the surface and the acrotelm is thin. The lower layers remain waterlogged with the associated much lower catotelm hydraulic conductivity of the order of 10^{-7} cm s^{-1} (Holden and Burt, 2003b).

Sheep in particular were observed to be affected by the waterlogged surface as they avoid areas that are entirely waterlogged and are vulnerable to conditions such as footrot in the absence of dry land (Stewart and Lance, 1983). In addition these waterlogged conditions encouraged the growth of *Sphagnum spp.* over the other major habitat flora, *Eriophorum vaginatum* and *Calluna vulgaris*. *Eriophorum vaginatum* and *Calluna vulgaris* are possible forage for sheep and food and shelter for grouse respectively; *Sphagnum* is neither. Furthermore, grouse shooting requires ready access to the land by substantial teams of people, animals and often vehicles, and such access is much less practical to achieve in areas of *Sphagnum* bog than it is on heather moorland. Drainage was, therefore, perceived to improve land for grouse shooting both through improvement of the habitat for grouse and through improved access.

During the 1940s-1980s extensive networks of drainage ditches were installed across large areas of blanket peat moorland in response to government grants for “improvement” of the land for forestry and agriculture (SNH, 2006; Holden et al., 2004). The peak of blanket peat drainage is thought to have occurred in the 1970s. The process of drain cutting was conceived to increase the runoff from the upper layers of peat as a lateral drainage path is made available into the side wall of the drain thus lowering the water table around the drain. Radcliffe and Oswald (1988) estimated that of the approximately 8% of the UK that is covered by blanket peat moorland, approximately 75% has been drained.

When dug the drains are largely uniform (due to the use of the standard Cuthberston plough) in having a trapezoidal cross-section, 50cm deep, 90cm broad at the top and 40cm broad at the base. Drain networks vary from a few drains whose primary purpose was to modify an existing natural drainage pattern or reduce erosion, to extensive networks of drains of a branching or herringbone structure, where spacing between drains can be between 7m to 20m.

Despite the aims of drainage, Watson and O’Hare (1979) found no evidence for increased grouse numbers on drained bog, and Stewart and Lance (1983) found no documented evidence of any actual economic benefits from drainage. The failure of drainage programmes to achieve the desired results is manifested in two main ways.

Dense drain networks cause problems in themselves. From the point of view of grazing, sheep will avoid areas criss-crossed by numerous drains which are approximately 90 cm wide and thus represent substantial obstacles to them. Grazing patterns therefore change and sheep become harder to herd and manage. Sheep prefer drier land which is likely to occur close to the drain channel and in particular on top of the ridge of peat soil left alongside the channel by the plough. However, a tendency by sheep to congregate in these linear patterns will only cause greater erosion at the drain edges, increasing waterlogging once again (Stewart and Lance, 1983). Similarly for grouse, drains cause a problem especially during the vital nesting season. Flightless chicks often fall into drains and at this stage in their lives their plumage is not sufficiently waterproof to survive the ordeal. They are therefore unable to escape and usually drown. In densely drained areas this substantially reduces yields.

Furthermore, drains are often not successful at lowering the water table to a useful extent other than in the immediate vicinity of the drain meaning that an extremely dense drain network is required in order to reduce the waterlogging of the land to the extent desired (Gibson, 2006).

1.3.3 Peat drainage outside the UK

Drainage of peatland is also widespread outside the UK (Holden et al., 2004): Joosten (1997) states that approximately 60% of all European peatlands have been drained. However, the reasons for drainage differ. Peatlands outside the UK are rarely drained for game management but to alter peatland hydrology to improve the suitability of peats for forestry; for agriculture; or prior to harvesting peat. Cooper et al. (1991) stated that in Northern Ireland only 169 km^2 of a total 1190 km^2 of peat were undrained. In Finland where drainage is undertaken chiefly to lower water tables to enable afforestation necessitating very dense drainage networks (Holden et al., 2004) 57 000 km^2 of peatland have been drained since the 1930s (Joensuu et al., 2002).

In other parts of the world, drainage has been shown to have serious environmental consequences. A recent report by DELFT Hydraulics and Wetland International (Hooijer et al., 2006) describe the extent of peatland drainage and burning in Indonesia where a key and increasing motivation for drainage is the use of land for the production of bio-fuels. Of 210 000 km^2 of peatland in Indonesia, 90 000 km^2 are currently drained. The decomposition of peat caused by this leads to annual CO_2 emissions from peat degradation in Indonesia alone of around 2000 Mt (Hooijer et al., 2006).

Peatland protection and restoration programmes are also widespread in several countries outside of the UK such as Ireland (Dail Eireann, 1998), Canada (Waddington and Price, 2000), Estonia, Sweden and Finland (Vasander et al., 2003). However, the magnitude of drainage such as that described by Hooijer et al. (2006), together with current biofuel subsides; mean that globally the effects of new drainage seem likely to greatly outweigh those of current peat restoration projects.

1.3.4 Hydrological effect of drainage

The key aim of peatland drainage in the UK was to lower the water table in the peat resulting in a firmer surface more suitable for grazing, walking and other access. However, due to the low hydraulic conductivity of peat and the often low relief of the areas over which they are found the water table is generally not found to drop in the manner which was originally desired (Stewart and Lance, 1991).

Studies dating back as far as the eighteenth century have described peatlands as storing water in a similar manner to a sponge, soaking up water during storms and releasing it gradually over a significant period of time, thereby reducing flow peaks and sustaining baseflows (Turner, 1757). However the opposing view has been demonstrated by many more recent studies, showing that the water table rarely drops far enough in blanket peats that substantial storage capacity is available to attenuate flood peaks (Eggelsmann, 1971). This supports observational data that blanket peats produce a great deal of run off with extremely flashy hydrographs and relatively small baseflow contributions (Evans et al., 1999).

A flashy hydrograph may seem to suggest that waterlogged peats can easily be made to give up their water and that drainage should be successful, probably adding further to the flashy nature of the hydrograph response. However, many studies have shown that the vast majority of flow in blanket peats takes place over the surface and through the upper few cm (Holden and Burt, 2003b). Drainage may well play a part in increasing the flashy nature of the hydrograph response by increasing surface runoff as overland flow has only to travel as far as the nearest drain channel before it is rapidly removed, with flow in drains being even faster than flow over the peat surface or through the near surface layers. However, the implication of this near-surface dominated flow is also that the water table drawdown caused by a drain may not extend a great distance laterally from the drain. Any drop in the water table caused by lateral flow from the peat layers into the side walls of a drain channel will be slow enough that it is easily replenished by infiltration from above. Sillins and Rothwell (1998) also made the point that drainage is likely to lead to some subsidence and compaction of the peat layers, which will decrease hydraulic conductivity and increase water retention, acting against the aim of drainage by limiting flow of water into the drain channels.

Any lowering of the water table by drains may cause additional carbon production. With respect to DOC, Clausen (1980) found that concentration increased upon drainage and Mitchell and McDonald (1995) showed that at a catchment scale, the most densely drained areas were the largest sources of DOC. Increased soil CO_2 respiration has been observed upon drainage of peatlands by Silvola et al. (1985) and Komulainen et al. (1999) showed that the soil respiration of CO_2 decreased following restoration of the water table at a peatland in Finland. Nykanen et al. (1995) found that N_2O emissions were higher in areas of drained peatland in Finland compared to virgin fen land. Sirin et al. (2008) found that drainage of nutrient rich peatlands leads to a rise in N_2O. Methane however exhibits the opposite behaviour: Tuittula et al. (2000) have shown that upon restoring a cut away peatland there was a significant increase in CH_4 flux. Glatzel et al. (2012) also found that for rewetted fen land in Germany CH_4 release had increased and that this increase could be related to changes in the water table. A similar increase in CH_4 was found in California by Hatala et al. (2012) when deltaic peatlands were flooded.

This reported increase in CH_4 following peatland rewetting would have implications for attempts to mitigate climate change as methane is a greenhouse gas. This thesis considers the effect of blocking on water colour and DOC and as such the monitoring and study of the effect of blocking on methane release falls outside the scope of this study, although due to its global significance its importance should be noted.

1.4 Peatland restoration

The blocking of these drainage channels has been considered as a means of peat restoration. It is believed that colour release from these areas can on the whole be related to changes in water table depth in the soil profile (Tipping et al., 1999). Although the excavation of drainage channels was not found to decrease the water table in the manner which was originally desired (Stewart and Lance, 1991), peatlands are sensitive systems and even moderate changes to water tables might influence their chemistry and the cycling of carbon. An increase in the depth to the water table increases the area of oxidation in the soil and it is within this oxidised area that DOC is produced. The greater the drawdown of the water table the larger the area of oxidation and so greater production of DOC and water colour. Thus, by reducing this area of oxidation, by preserving a high water table, it is believed that DOC release can be limited.

Several different methods of drain blocking have been used along with a variety of materials. A range of materials and methods have been reviewed by Armstrong et al. (2009). Plastic or wooden dams can be used to great effect and have been recorded to reduce mean flow velocity by three orders of magnitude (Holden et al., 2005). Drains can also be blocked using heather bales or peat dams. These dams have been recorded to reduce mean flow by two orders of magnitude compared to open drains (Holden et al., 2005). The most common method of blocking in Upper Teesdale is the use of peat dams. Blocks of peat are cut from areas between drains and placed in the drain (known as the “cut and shut” method). The choice of blocking method used is often influenced by the location of the site, the natural wetness of the bog, the size of the drain to be blocked and the slope of the site. The construction of the dam creates much slower flow velocities which encourage the deposition of sediment and promote re-vegetation which in turn helps to trap further sediment.

Given the recent trend in drain blocking in the UK and the potential impact on water colour and DOC a number of studies have been undertaken to examine the effects. Gibson (2009) monitored water quality and hydrological data at several locations across upper Teesdale, North Pennines, where drains were either blocked or left unblocked. It was found via fingerprinting surveys that drained areas are indeed a major source of DOC to the water treatment works. The blocking of drains caused a decrease in the depth to the water table within peat soils and significant decreases in flow through the drain and significant decreases in particular organic carbon (POC) were observed. In terms of water colour export a 20% decrease was recorded. However, this decrease in water colour export was dominantly caused by the decrease in water yield from the blocked drains rather than a decrease in DOC concentration– although a significant effect, Gibson et al. (2009) observed only a 1% decrease in DOC concentration.

Wallage et al. (2006) demonstrated that drain blocking decreased water colour and DOC concentration by between 60% and 70% in soil water sampled from piezometers in the vicinity of blocked (5 years prior to monitoring) and unblocked drains at one site in northern England. However no samples from runoff were measured. In contrast to the studies by Wallage and Gibson, Worrall et al. (2007) found water colour to be slightly higher in blocked drains compared to unblocked drains. However, the work was limited in that monitoring only began 1 month prior to blocking and ceased 8 months after meaning that the results may reflect immediate impacts of disturbance rather than the longer term trend. Equally, Worrall et al. (2007) did show that flux of DOC would decline post blocking because although DOC concentration rose there was a greater decline in stream flow upon blocking.

Armstrong et al. (2010) combines data from an UK-wide survey of blocked and unblocked drains across 32 study sites and intensive monitoring of a peat drain system that has been blocked for 7 years. It was found that water colour and DOC concentration was significantly lower in blocked drains with a mean difference of 28% compared to the open drains. However, this pattern was not consistent across all sites with the intensively monitored site showing no significant difference in DOC concentration.

Wilson et al. (2011) considered the effect of ditch blocking on water quality, peat erosion, flow rates and flood risk, and nutrient fluxes at a landscape scale in the Lake Vyrnwy catchment in mid Wales for a period both pre and post blocking. The E4:E6 ratio, a measure of humification being the ratio of humic acids to fulvic acids (Thurman, 1985), was found to increase post drain blocking while the specific absorbance decreased indicating as Wilson et al. (2011) stated "*that DOC released from blocked drains consisted of lighter, less humic and less decomposed carbon*". Whilst concentrations of DOC showed slight increases in drains and streams after blocking, instantaneous yields of both DOC and POC decreased over the first year post-blocking. For the same catchments Wilson et al. (2010) found increased water retention and higher water tables after drain blocking. The study also demonstrated the importance of small and large scale topography in determining the degree of these responses. The increases in water storage after restoration produced lower discharge rates observable at the level of both drains and hill streams; as well as greater water table stability, reduction in peak flows and increases in water residency after rainfall. The study showed strong catchment scale differences in response, and a very gradual recovery of water tables, both of which Wilson et al. (2010) states "*highlight the need for more studies to be carried out at the landscape scale and over longer time periods*."

Grand-Clement et al. (2012) found DOC export to decrease when considering the effects of drain blocking on water quality on Exmoor, South West England. High resolution monitoring of selected ditches of various sizes was employed and water samples analysed for DOC, POC, pH and colour. These variables were identified as critical, both in terms of carbon cycling and for costly water treatment that currently takes place downstream. Results were examined spatially in relation to drain sizes and magnitude/frequency of event.

Ramchunder et al. (2012) considered the effects of drain blocking on the biodiversity of the drains. The study demonstrated changes in the structure of stream benthic macroinvertebrate assemblages linked to increases in benthic particulate organic matter and suspended sediment following peatland drainage. However, these effects were reversed following catchment-scale restoration by drain-blocking. Ramchunder et al. (2012) states that "*drain-blocking therefore appears to benefit not only peatland soil, vegetation and hydrological ecosystem services but also stream water quality and biodiversity*". The importance of pre- and post-blocking monitoring of streams is also stressed.

In addition to this UK based research, studies by Glatzel et al. (2003) and Waddington et al. (2008) have been performed in Canada. Waddington et al. (2008) found that DOC concentration increased after restoration, however, the drains in the study were only hydrologically blocked at one end and were infilled with loose vegetation and covered with peat meaning that comparison with the UK studies is limited. Furthermore, straw and *Sphagnum* diasporas were added to the peat surface and this was reported to increase decomposition. Glatzel et al. (2003) investigated the DOC concentration response to varying restoration methods including the blocking of ditches. However, the morphology of these ditches was very different and only partially blocked so comparison again with UK studies is not possible. Höll et al.

(2009) considered the characteristics of dissolved organic matter following 20 years of peatland restoration for a peatland in South-West Germany. The study demonstrated that DOC concentration levels were lower in peats where the water table was close to the surface compared to peats where the water table was around 30cm from the soil surface.

1.5 Previous study limitations and the issue of scale

There are a number of common limitations across all these studies. None of the studies considered above included sufficient controls over a sufficient period of time. Although a number of the studies above did consider pre-intervention monitoring of a drain prior to blocking none of them considered more than 3 months of pre-blocking data (Gibson et al., 2009). No study had pre and parallel controls across a complete seasonal cycle. Secondly, the majority of the studies measured at the scale of the drain, but not at larger scales. With the exception of Wilson et al (2010, 2011), who indicates that further research is need to consider the effects of blocking at landscape scales, previous studies have considered the effect of blocking on an individual drain scale and then have employed models to scale up this effect to catchment scales. A study of the Whitdendale catchment in the Forest of Bowland (Worrall et al., 2007a) demonstrated that the water colour record was affected by drain blocking at individual drain scales yet this study found no evidence in the DOC record of an effect at a catchment scale.

When considering the effect of drain blocking at larger scales several issues which may affect drain blocking efficiency must be considered. Firstly it is likely that at some point that a drain will cut across slope. As the drain is crossing the slope the water in the channel will tend to flow down slope under the force of gravity taking any DOC with it and so bypassing the blockages and entering the surface waters of the catchment elsewhere. The bypassing of flow around the blockages means that any effect of drain blocking seen on an individual drain scale may be lost when the effects are examined at catchment scales.

Secondly in order to assess the impact of drain blocking upon DOC concentration and flux it is necessary to assess whether other effects could be contributing to a change in DOC concentration that are not due to the blocking. These other effects would include the natural degradation of DOC in the stream waters; and any dilution effects that would occur as the water moves upscale. These effects are important limitations on assessing the extent of any benefits of drain blocking and when considered together with the calculated DOC budgets any reduction in water colour observed post blocking may be suppressed. Cannell et al. (1999) estimated that the annual loss of carbon from UK rivers is of the order 0.68 Mt C/yr and Aitkenhead et al. (1999) suggested that the majority of this carbon will be lost from peatlands. The fluvial flux of carbon from peatlands represents between 35 and 50%

of their total carbon flux (Dawson et al., 2002). It is considered that the majority of this apparent carbon loss occurs at a scale of less than 1 km^2 (Moran and Zepp, 1997). Within low-order streams there are a range of processes that could remove, degrade or add DOC to the flux. Specifically, this study considered the effects of the biodegradation, photodegradation and the addition of dissolved carbon dioxide (a review of these processes can be found in chapter 3).

Thirdly, the blocking of the drains causes water to be held back in the peat which in turn leads to a higher concentration being present such that when flow does occur it is of a higher concentration leading to a larger colour release event. There is consequently a need to examine the wider effect of drain-blocking at a catchment scale to ensure that what is observed for one drain transfers to the whole catchment. This study, therefore aims to assess the impact of drain blocking on the DOC release from a chain of zero and first order drains in a blocked and unblocked condition while maintaining sufficient pre- and post-intervention controls.

1.6 Aims and Objectives

This thesis aims to test the hypothesis that the blocking of drainage channels is an effective means of reducing DOC runoff at the catchment scale. It also aims to identify the most appropriate methods for widespread peat restoration.

This can be broken down into a series of specific objectives:

1. Measure the water colour budgets for a nested series of catchments where drains have been blocked in comparison to catchments where drains have not been blocked.
2. Monitor the water balance and storage through the blocked and control catchments.
3. Fingerprinting flow pathways for water and water colour within blocked and unblocked catchments.
4. Assess to what extent DOC is lost from the system by degradation processes.
5. Evaluate to what degree the blocking of drains is beneficial on a large scale across blanket bog and investigating the ideal timescale for monitoring restoration of the peat mass.

2. DOC budgets at catchment scales

2.1 Introduction

This chapter aims to investigate the influence of drain blocking on the dissolved organic carbon (DOC) export from a series of nested catchments in Upper Teesdale. More specifically this chapter aims to discuss the issue of scale to establish whether any benefits of drain blocking recorded on an individual drain scale can be transferred to catchment scales. The chapter will firstly introduce the study sites and provide a description of the monitoring equipment found there before discussing the methods used to calculate the DOC budget and its results. The budgets will then be compared and contrasted to determine whether differences between blocked and unblocked catchments can be seen.

The catchments are located on blanket bog in the Upper Teesdale area of the North Pennines, England. The first two catchments are located on Cronkley Fell which forms part of the Holwick Grouse Shooting Moor run by the Strathmore Estate. Here two catchments were monitored, a control catchment where the drains were left open for the duration of the study and an experiment catchment where drains were monitored for 12 months prior to blocking and 12 months after. The monitoring of two individual drains, one blocked and one unblocked on the Wemmergill Southside shooting estate has also taken place. A pristine catchment at Atkinson's Peat Moss owned by the Raby Estate has also been monitored.

2.2 Restoration of drained peat

Extensive drainage of UK peatlands has been associated with dehydration of the peat, an increase in water colour and a loss of carbon storage. It has been considered that the blocking of these drainage channels represents a means of peat restoration and a way of reducing DOC losses to surface waters. As discussed in chapter 1 it is hypothesised that colour release from these areas can on the whole be related to changes in water table depth in the soil profile. An increase in the depth to the water table increases the area of oxidation in the soil and it is within this oxidised area that DOC is produced. The greater the draw down of the water table the larger the area of oxidation and so greater production of DOC and water colour. Thus, by reducing this area of oxidation, by preserving a high water table, it is believed that DOC release can be limited.

2.3 Study Sites

A detailed sampling programme has taken place from August 2007 to May 2010 in a series of blocked and unblocked catchments. All are situated on upland peat moor in Upper Teesdale in the northern Pennines, England (Fig 2.1).

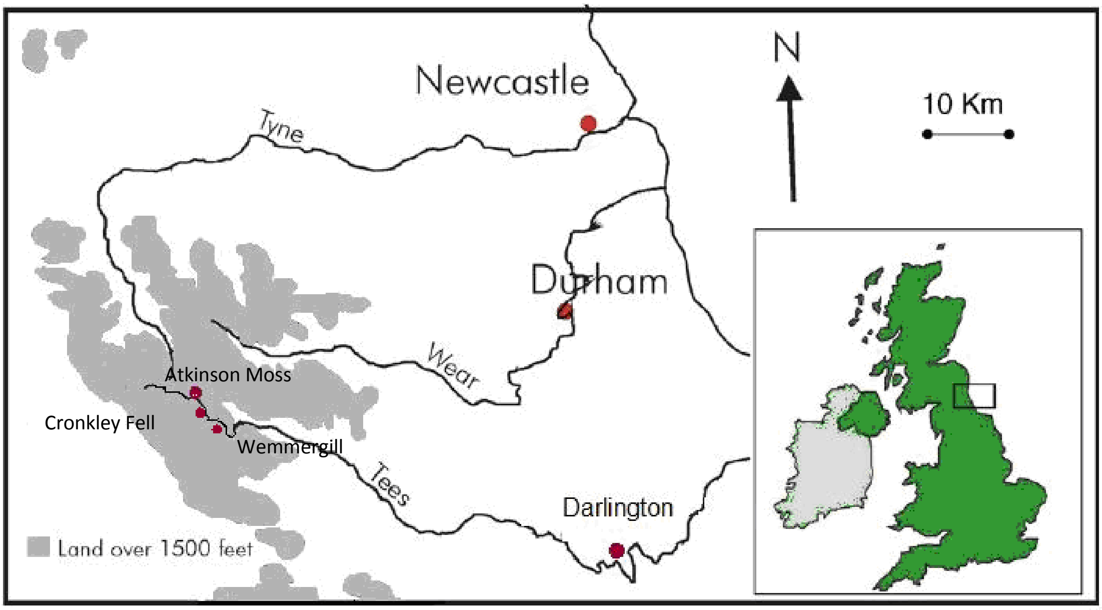


FIG. 2.1: Location of Monitoring Sites in Upper Teesdale

Atkinson Moss Peat Bog (pristine catchment)	NY80560/35000	(540m)
Cronkley Fell, Control Catchment (unblocked)	NY83140/27284	(520m)
Cronkley Fell, Experimental Catchment (blocked)	NY83800/26996	(570m)
Wemmergill Experimental (blocked)	NY88626/20101	(390m)
Wemmergill Control (unblocked)	NY86383/20028	(420m)

2.3.1 Cronkley Fell

Two catchments are located on Cronkley Fell, within the Strathmore Estate above the village of Holwick (Fig. 2.1). The area is managed for grouse shooting and sheep grazing with large areas being managed by prescribed, rotational burning. The underlying experimental design is of two sets of nested catchments. The first catchment is an unblocked control catchment left unblocked throughout the entire study (national grid reference NY 83140/27284) at an altitude of 520m above sea level. The second catchment, the experimental catchment, (national grid reference NY83800/26996) is at an altitude of 570m above sea level. The second nested catchment was blocked one year into the study. The two sets of nested catchments share a watershed. The underlying geology of both sets of nested catchments is a succession of limestones of the Great Scar limestone group. The vegetation is dominated by *Eriophorum spp.* (cotton grass), *Calluna vulgaris* (heather) and *Sphagnum spp.* (moss). The poor drainage has led to the development of extensive blanket peat of depths up to 1.5m. The catchments lie within an area of peat that has been drained extensively and extremely densely with drain spacing varying from 20 m to 7m. The majority of drains on Cronkley Fell have been blocked using peat dams via the cut and shut method (Worrall et al., 2008).

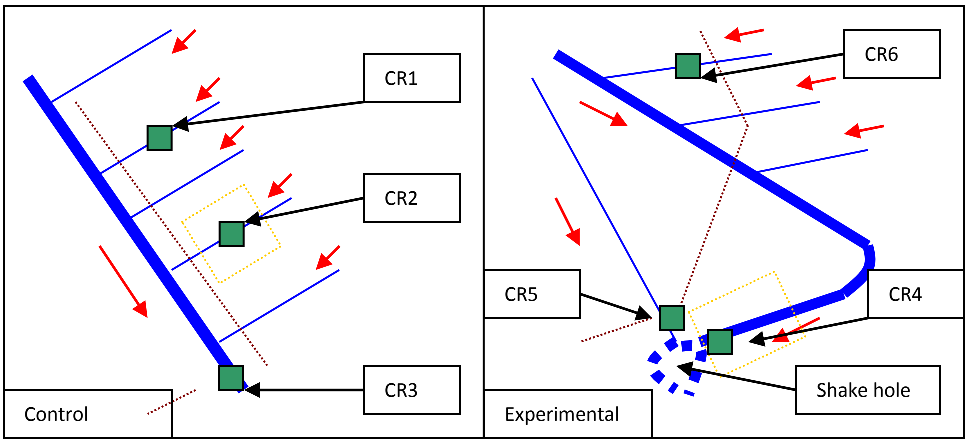


FIG 2.2: Schematic diagram of monitoring site layout on Cronkley Fell

KEY 🟩 Monitoring site
▬ First order stream
— Zero order stream
→ Flow direction
┈ Soil water dipwell network
┈ Run off trap network

Both catchments are set up such that individual drains can be monitored within the context of a larger catchment. For the control catchment two individual zero order drains (CR1 and CR2 - Figure 2.2) were monitored and the first order drain (CR3) into which the two zero order drains flowed. Zero order drains are defined as those where the base of the drain lies in peat and has no feeder drains. First order drains are those which the zero order drains flow into. They are generally larger in size with higher water yields, more complex hydrographs and the base of the drain may not be entirely within a peat soil. CR1 has a catchment area of 0.230 km^2, a drain depth of 72 cm and cuts perpendicularly across a slope of 20º. CR2 has a catchment area of 0.215 km^2, a drain depth of 60cm and cuts perpendicularly across a slope of 15º. CR3 has a catchment area of 0.750 km^2, a drain depth of 58cm and runs parallel to a slope of 10º. The base of the drain at CR 3 interacts with the mineral substrate. Estimates of catchment areas were calculated by GPS readings of the water shed based on both field observations of the water shed location and detailed Ordnance Survey maps of the area.

For the experimental monitoring location the catchment is set out in a similar pattern to the control catchment in that monitoring takes place on two zero order drains (CR5 and CR6 in Figure 2.2) and one first order drain (CR4). CR6 flows directly into CR4, however due to the natural layout of drains on the ground CR5 does not flow directly into CR4. CR5 runs parallel to the sites and is representative of a zero order drain due to its small cross sectional area, a lack of any feeder drains and the drain being entirely in peat. It runs parallel to the slope of 15º, has a catchment area of 0.443 km^2, and a drain depth of 75 cm. CR4 has a catchment area of 0.715 km^2 and runs perpendicular to a slope of 14º. It has a drain depth of 80 cm. CR6 has a catchment area of 0.305 km^2 and runs perpendicularly to a slope of 10º. It has a drain depth of 72 cm.

FIG 2.3: Cronkley Fell looking, north west to the Cowgreen Reservoir, October 2007

The area is subject to approximately 2000 mm of rainfall per year. Temperatures are seen to vary from a maximum recorded temperature of 20ºC in the summer to a minimum of -10ºC in the winter. The winters of 2007-2008, 2008-2009 and 2009 - 2010 saw heavy snow fall with depths of snow up to 40cm. This caused problems accessing the site leading to gaps in the data set. Also heavy snow delayed the blocking of drains on the experimental catchment with the drains due to be blocked in December 2008 and actually being blocked in March 2009.

2.3.2 Atkinson's Peat Moss

Atkinson's Peat Moss lies to the North of the Cowgreen Reservoir above the village of Harwood and forms part of the Raby estate (Fig. 2.1 - national grid reference of NY80560/35000) at an altitude of 540m above sea level and a catchment area of 0.905 km^2. This is a pristine catchment in that the area has undergone no artificial drainage methods. The site falls within a Black Grouse protection zone and as such has undergone no grazing for the last 15 years. Vegetation at this site is dominated by *Eriophorum spp., Sphagnum spp. and a range of grasses (Agrostis and Nardus)*: there is little or no *Calluna vulgaris*. The site is covered by deep blanket bog with peat soils reaching a depth of 1.8m. The peat is underlain by a succession of limestones of the Alston and Yoredale groups.

Monitoring on this site occurred on a natural stream that flows across the locality, the base of which is entirely in peat soil. The site has a gentle slope of 5° which the stream runs parallel with. The site is cut at the north by a busy main road. During the winter months samples are often contaminated with chloride and sulphate as a consequence of road gritting.

Fig 2.4: Atkinson's Peat Moss, looking south down Teesdale, October 2007

Climatic conditions at Atkinson Moss are similar to those found on Cronkley Fell with an average rainfall of 2000 mm per year. Temperatures are seen to vary from a maximum recorded temperature of 20ºC in the summer to a minimum of -10ºC in the winter. The site is often covered by heavy snow in the winter, however due to the site's close proximity to the main road access is affected to a lesser degree than at Cronkley Fell.

2.3.3 Wemmergill

Two individual drains were monitored at the Wemmergill site, an unblocked control drain and a blocked experimental drain (Figure 2.1). This site forms part of the Wemmergill Southside Shooting Estate and lies to the west of the Selset reservoir. The experimental drain (grid reference of NY88626/20101) is at an altitude of 390m above sea level with a catchment area of 0.515 km^2. It runs parallel to a gentle slope of 4^o with a drain depth of 73 cm. The control drain (grid reference of NY86383/20028) is at an altitude of 420m with a catchment area of 0.351 km^2. It runs parallel to a slope of 11^o with a drain depth of 59 cm. The vegetation is a mixture of *Calluna vulgaris*, *Sphagnum spp.* and *Eriophorum spp.*. The underlying geology is a succession of Carboniferous sandstones, siltstones and limestones. The area is actively managed for grouse shooting with large areas of *Calluna sp.* being burnt in rotation. The area is also used for sheep grazing.

FIG 2.5: Wemmergill, looking North, February 2008

The climatic conditions at Wemmergill again vary very little to those experienced on Cronkley Fell and Atkinson Moss with an average rainfall of 2000mm per year being recorded. The average temperature is on average 2ºC higher at Wemmergill than Cronkley Fell and Atkinson Moss due to the lower altitude. The temperature is seen to vary from a maximum recorded temperature of 22ºC in the summer to a minimum of -7ºC in the winter. In winter the site is often covered with snow limiting access to the sites during these periods.

2.4 Water Sampling programme

To allow DOC export budgets to be calculated a detailed sampling programme was undertaken from August 2007 to May 2010. The sampling programme was designed to collect as much data as possible in order to calculate the DOC budget directly through the calculation of the product of flow and concentration. To achieve this flow was monitored semi continuously using a V- notch weir with stage measurement by pressure transducers. DOC concentration was not monitored continuously (for instance by turbidity monitoring) but by frequent automatic sample collection and laboratory analysis.

2.4.1 Sample Collection

Each of the nine sampling localities was installed with an automatic water sampler (5 Buhler-Montec Xian 1000 samplers, 2 ISCO 3700 Portable samplers, 2 Aquamatic Aquacell P2 samplers). Each sampler has an automatic distributor and 24 500ml sample bottles. The samplers are designed to take samples at preset intervals via an indirect pump mechanism which reduces the chance of equipment failure in dirty water and also reduces cross-contamination of samples.

The samplers were fitted with a hose of sufficient length that the sampler unit could be situated away from the stream channel to avoid the risk of it becoming flooded during high flow events. The hose was carefully place at the base of the drain on top of a flat stone to ensure that water samples were taken from the bottom of the stream yet were not block by the loose sediment found there. A sample is taken by first flushing the sample chamber and hose with air to remove any water from the previous sample. The air direction is then changed and the water is pumped up the hose into the sample chamber and distributed into the appropriate sample bottle.

The samplers were preset to take water samples at least every 24 hours. Periods of increased sampling have also been conducted (spring and autumn of 2007, 2008, and 2009) during the spring and autumn flushed periods when samples were collected every 8 hours. During the start of the grouse shooting season (mid to late August) and the grouse fledging season (May to mid June) samples were taken every 24 hours due to site access restrictions. Gaps in the sampling record occurred due to failure of equipment, the freezing of drains in winter and during dry periods in the summer when there was little or no water flowing in the drain.

The monitored sites were visited to collect the water samples usually the day before the programmed end of the sampling run to minimise breaks in the data record. For example a sampler running an 8 hour sampling routine would fill the 24 bottles in 8 days thus sites would be visited every 7 days. A sampler running a 24 hour sampling routine could run for over 3 weeks before sample collection is necessary. However the implication is that samples were often left in the sample bottles for up to 3 weeks. Laboratory tests conducted in the same research group on stability of DOC samples kept in the dark (as in the storage base of the sampler) and at field temperatures showed no significant change ($P<0.05$) in DOC concentration over these periods (F. Worrall, pers. comm., unpublished data).

In the field, water samples were decanted into two 30ml sterolins. The samples were then transported back to the laboratory where they were frozen to prevent contamination or decomposition of any organic matter. If samples were unable to be frozen they put in the refrigerator prior to analysis the following day.

2.5 Hydrological monitoring programme

2.5.1 Flow monitoring methods

Flow from each of the nine selected catchments was monitored at each locality using half 90° V-notch weir plates, with water depth over the weir measured by a pressure transducer fixed to the weir and calibrated upon each site visit. Evans et al. (2001) states that "*The flow regime in small peatland streams is expected to be extremely flashy with peak flows being as much as two or even three orders of magnitude higher than baseflows*". This method enables high resolution low flows to be measured while also being capable of handling larger flows.

The method is susceptible to errors at discharges below 0.02 Ls^{-1} where any errors in the measurement of stage with a weir installation become relatively more significant. Under such low conditions a tipping bucket gauge would be more appropriate however under high flow conditions it is likely most tipping buckets would be overwhelmed. Tipping buckets require water to be channelled from the drain into the gauge and then leave the gauge to drain away. This needs a sufficient hydraulic head to keep the water flowing and due to the only gentle slope of the drains at the field sites the installation of this type of device would have been impractical. Therefore V-notch weirs were selected as the best compromise.

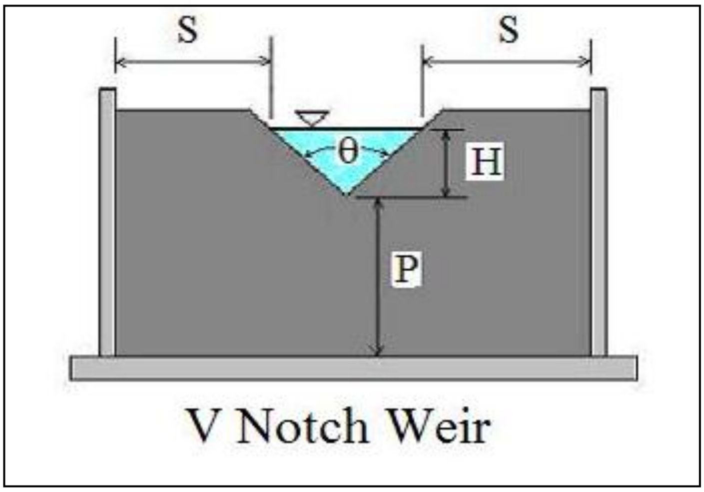


Fig 2.6: Diagram of V-Notch Weir (Bengston, 2010)

Flow for a V-notch weir can be calculated from depth data using the following equation:

$$Q = C_e * \frac{8}{15}\sqrt{2g} * \tan\frac{\theta}{2} h^{2.5}$$

Where:

- **C$_e$** is the discharge coefficient for the weir, taken as **C$_e$** =0.578 for the half-90° weirs.
- **θ** is the angle of the V-notch in degrees
- **g** is the acceleration due to gravity, taken as 9.81ms^{-2}
- **h** is the depth of water over the weir in metres
- **Q** is discharge in m^{3}s^{-1}

Derivations of the equation are to be found in ISO (1980).

The weirs were constructed from marine plywood and installed across the drains such as to extend at least 30 cm beyond the sides and bottom of the drains to eliminate bypassing flow. Manual checks on the accuracy of the v-notch weirs were performed in the field.

2.5.2 Stage Measurement

The depth measurement was achieved in the drains using pressure transducers to sense the depth of the water over the weir v-notch. Pressure transducers (Campbell Scientific PDCR1830, details at Campbell (2007)) were fixed directly to the back of the weir plates towards the side of the plate such that the transducer was not affected by the turbulent water passing through the v-notch. The transducers were connected to dataloggers (CR1000, CR800, CR10X and CR510, Campbell Scientific, details at Campbell (2007)) and were programmed to sample every 10 seconds with the average reading being recorded every 15 minutes.

Solar panels were installed at each monitoring location to provide back up energy to a 12 volt lead acid battery which powered the datalogger. The dataloggers could record approximately 3 months of data before the data records need to be downloaded. Data was downloaded on every field visit to PDA using Campbell Scientific PC200W software (Campbell, 2007).

The precision and repeatability of measures made by these components during normal flow conditions is high (precision 0.1%, repeatability 0.1%). However, problems occurred in the winter months when drains froze over. The freezing of drains would cause unreliable depth measurements as the pressure difference under the frozen water surface was too large or if the drain froze at transducer height this would lead to an extreme rise in pressure at the sensor head causing the head of the sensor to expand with the ice and the quartz crystal to crack. The main cause of gaps in the flow record during the winter months is due to the loss of pressure transducers during drain freezing.

The pressure transducers suffered further damage through wildlife such as rabbits and sheep gnawing through the cables. Cables were buried beneath the surface of the peat to try to prevent damage, however inevitably some components must be placed on the surface to enable proper use of the sensor. Furthermore, gaps in the data were caused by failure of the datalogger. This occurred either due to premature failure of the datalogger power supply or extreme weather conditions causing water damage to the datalogger. The dataloggers were encased in plastic boxes and packed with silica bags to absorb water moisture. However, during the winters of 2008-2009 and 2009-2010 datalogger boxes were under approximately 40 cm of snow (gamekeeper pers. coms.) for over 2 months. When snow melted the boxes were flooded causing irrecoverable damage to the datalogger and its electronics.

2.6 Laboratory Analysis

Samples were analysed in the laboratory for DOC concentration to calculate DOC export and other characteristics to assess character of the source (data from these additional analyses is presented in chapter 5, “Chemical tracing and flow pathways”). Actual DOC content was calculated using the colorimetric method of Bartlett and Ross (1988). Due to the large number of samples produced each week actual DOC concentration was measured only on a subset of samples from each site from each sampling visit. Absorbance was measured on every sample and a calibration curve for every site between absorbance at 400nm and DOC concentration was produced in order for a DOC concentration to be calculated for each water sample.

2.6.1 Sample preparation

All frozen water samples were allowed to defrost over night with the sterolins stood upright to allow sediment to settle. The analysis of samples for both absorbance and DOC concentration was carried out on filtered samples. Water samples were filtered through 0.45 µm cellulose nitrate syringe filters and placed in clean sterolins.

2.6.2 Absorbency

Sample absorbency was measured at 400, 465 and 665 nm on filtered samples using a UV/VIS spectrophotometer (Jenway 6505 UV/VIS Spectrophotometer). Absorbency data can be used as a quantitative measure of water colour. The absorbance of a sample at 400nm generally has a linear correlation to the concentration of humic matter (Packham, 1964). Absorbency measurements at 465 and 665 were taken in order to calculate the E4/E6 ratio of the samples, the E4/E6 ratio being the ratio of these absorbency values (465nm/665nm). E4/E6 ratio is a measure of humification being the ratio of humic acids to fulvic acids (Thurman, 1985). Samples were placed in clear cuvettes and the spectrophotometer calibrated using a blank sample of DI water. The spectrophotometer was regularly calibrated and the zero point checked after measurement of every sample at each wavelength.

2.6.3 DOC Concentration

This study used the colorimetric method of Barlett and Ross (1988) to calculate DOC concentration. This method, while not as sensitive as C analyser methods, requires no expensive equipment and makes analysis possible on samples of limited size such as extracted soil solutions. Access to a TOC analyser was not available for this study. It relies on measuring the loss of colour by a Mn(III)-pyrophosphate complex as Mn(III) becomes reduced by organic C in the presence of concentrated H_2SO_4. The method is applicable to 1 ml samples containing 0.08 to 4.0 µmol of organic C and is practically free of interferences in aerobic solutions. A 1 ml aliquot of sample is used with 0.5 ml each of H_2SO_4 and a manganese complex. Samples are left to incubate for 18 hours. The absorbance is then determined at 495 nm. Calibration standards of 60, 30 and 15 mg C/l carbon are produced from a diluted oxalic acid stock solution. These standards are used to create a calibration curve from which the 495 nm absorbency data can be converted to DOC concentration. This method was found to have an error of approximately ±2 mg/l DOC. Absorbency data at 400 nm is used to create a calibration curve with actual DOC and this is then used to calculate DOC content for all other collected samples from the absorbance measurements.

2.7 DOC Budget Calculation

In order to assess the change in DOC export related to drain blocking the results from the sampling programme were used to create a detailed DOC budget for the study catchments.

The derivation of a total budget from non-continuous measurements involves interpolation or extrapolation of concentration and flow measurements to produce a continuous export estimate, which can be integrated to estimate total export. Phillips et al. (1999) reviews a range of proposed methods for this in reference to sediment loads (for example, Verhoff and Yaksich, 1982; Phillips et al., 1999; Olive and Rieger, 1988). Littlewood (1995) suggests that these are generally applicable to mass load estimates, including DOC load.

All the methods have an inherent error associated with them. Sources of error can also occur due to the varying sampling frequency. Load estimation methods assume a continuous flow record (or a short interval non-continuous record such as every 15 minutes) and a non-continuous concentration record. Extrapolation methods first extrapolate the non-continuous concentration record into a continuous synthesised record based on a regression relationship or calibration curve between flow and concentration. This synthesised record is then used to calculate flux for the continuous flow record.

Interpolation methods estimate the concentration at any particular point in the flow record by interpolation of the nearest actual concentration measurement without necessarily attempting to explain the variation of the concentration between those points in terms of flow or any causatory factor.

Littlewood (1995) summarises a range of common interpolation methods:

$$Load = K\left(\sum_{i=1}^{n}\frac{C_i}{n}\right)\left(\sum_{i=1}^{n}\frac{Q_i}{n}\right)$$

“Method 1”

$$Load = K\sum_{i=1}^{n}\left(\frac{C_iQ_i}{n}\right)$$

“Method 2”

$$Load = K\sum_{i=1}^{n}\left(C_i\overline{Qp}\right)$$

“Method 3”

$$Load = K\left(\sum_{i=1}^{n}\frac{Ci}{n}\right)\overline{Qr}$$

“Method 4”

$$Load = K\frac{\sum_{i=1}^{n}CiQi}{\sum_{i=1}^{n}Qi}\overline{Qr}$$

“Method 5”

Where

Ci= instantaneous concentration (with “instantaneous” defined by the interval of the flow record)

Qi= instantaneous flow

n= number of samples in the record

$\overline{Qp}$ = the mean discharge between concentration samples

$\overline{Qr}$ = the mean discharge for the entire record period

K= conversion factor for the period of record

All these methods still require some instantaneous concentration value for each point of the flow record. Extrapolation and interpolation methods differ in how this instantaneous concentration estimate is developed from the non-continuous record. Extrapolation methods are less appropriate for species that have a strong seasonal component, such as DOC, as this seasonal variation will not be accounted for in the derived relationship between flow and concentration. This study uses “Method 5” (Littlewood, 1995) with instantaneous concentrations values taken as being equal to the most recent actual concentration sample. The DOC flux values were collated in to monthly and annual totals. DOC export was calculated by dividing the flux values by the area of each catchment. An average error of ± 0.002 tC/km^2 was recorded.

2.8 Statistical Analysis

This study aims to assess the impact that both scale and drain blocking have upon DOC concentration and DOC export thus the data was examined by analysis of variance (ANOVA). The ANOVA was used in a series of separate analyses. First, DOC concentrations from the monitored drains were considered along with the following factors: month of the year; site; drain blocking status; and the scale of the drain. The month factor has 12 levels, one for each month of the year, and the site factor has 9 levels one for each monitored site. The drain-blocking factor has two levels, blocked and unblocked. The scale factor has two levels, zero and first order. The second analysis was performed considering the relative DOC concentration. To negate any effects of the natural variation in DOC from year to year the DOC concentration of a blocked drain should be considered relative to the DOC concentration of an unblocked drain at the same scale in the control catchment. Relative DOC is calculated by the ratio of the monthly average DOC concentration of a blocked to the unblocked drain from the experimental and control catchment respectively. The factors considered were the same as for the first analysis. These two analyses were repeated with DOC export - export rather than flux is used so as to allow for the difference in the size of the study catchments. The analysis of DOC export again considers the month, blocking status, scale and site factors. When considering the analysis of DOC export, water yield from each drain in that month was also considered as a covariate. Wherever possible with any ANOVA interactions between factors are considered. Post hoc comparisons between factor levels were conducted using the Tukey test and the proportion of variance explained by factors and covariates were estimated using the ω^2 method (Vaughan and Corballis, 1969). In all these analyses factors, interactions and covariates were considered significant if they could be demonstrated to have a greater than 95% probability of not being zero.

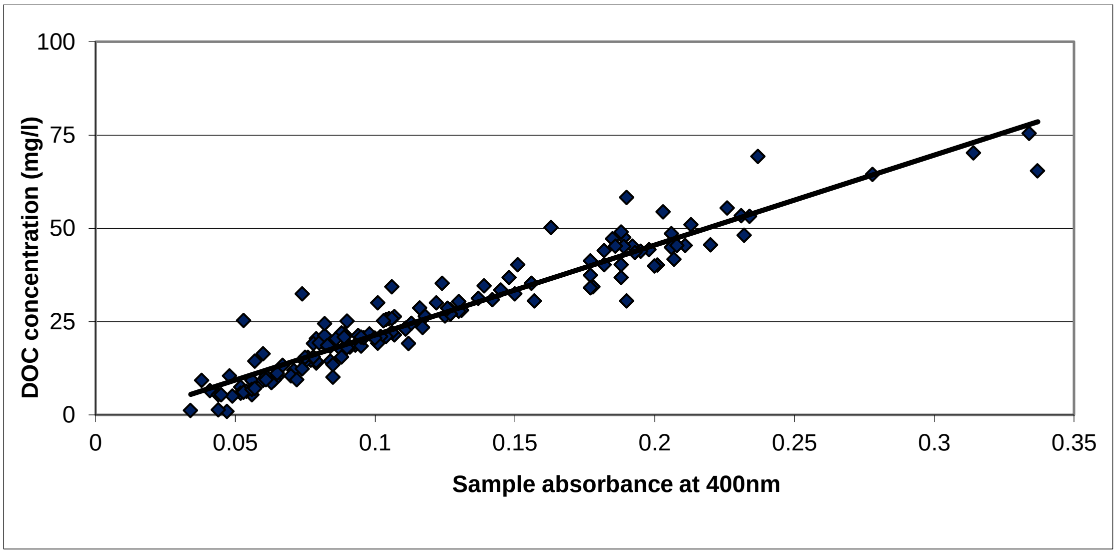
Any observed variation in DOC export trends between the blocked and unblocked catchment was examined by double mass analysis. Double mass curves allow variables to be examined to assess whether they are affected to the same extent by the same trends. The cumulative value of x is plotted against the cumulative value of y. A straight line would indicate that both variables are being affected to the same extent by a trend. Any break in the slope of the curve would indicate a change in trend for one of the variables (Searey and Hardistion, 1960). Double mass analysis was firstly used to examine the effect blocking has on relationship between water yield and DOC flux and secondly on the relative accumulation of DOC export between the blocked and unblocked catchments. This approach can have a higher sensitivity than trend analysis as the cumulative sum of a variable tends to have the effect of cancelling out random noise in the record.

2.9 Results

A high intensity monitoring program was conducted from Aug 2007 to April 2010. A total of 7232 water samples were collected from 48, 38 and 36 site visits to Cronkley Fell, Atkinson Moss and Wemmergill respectively. A total of 4332 samples were analysed from Cronkley Fell. Of these samples 1993 were from the pre blocking period and 2339 from the post blocking period. A total of 1626 samples were analysed from Atkinson Moss and 691 from the blocked drain on Wemmergill and 804 from the unblocked drain.

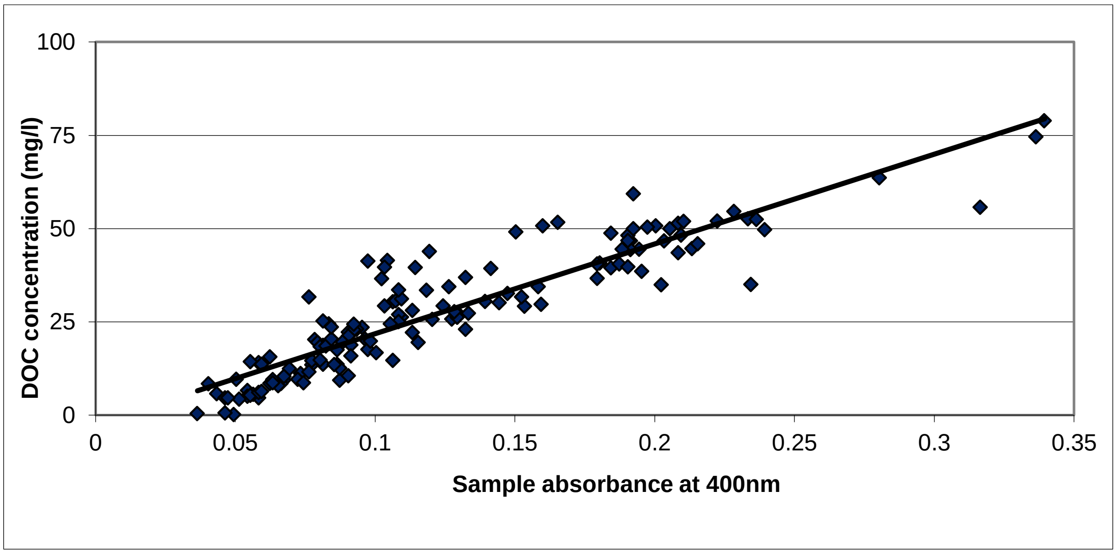
2.9.1 DOC calibration

The DOC concentration has been calculated on a total of 7232 water samples. Of these water samples 5424 (approximately 75%) had DOC concentration calculated directly by the colorimetric method of Bartlett and Ross (1988). The DOC concentration of the remaining 1492 samples was calculated from the use of a calibration curve between DOC concentration and the absorbency at 400 nm. DOC concentration calibration experiments were carried out on samples taken from all nine monitored drains. Those samples analysed for actual DOC concentration were selected to represent a range of flow, weather and seasonal conditions. A linear relationship was found between DOC concentration and absorbance at 400 nm across all sites (Fig. 2.7 - 2.17) however the slope of these calibration curves was found to vary by up to 33% thus different calibration curves were created for each individual drain. Wallage et al. (2006) suggests that a stable relationship between the two variables may not be a robust assumption and that in some circumstances the relationship between colour and DOC concentration may exhibit variation with time since blocking of a drain. As this study considers a range of unblocked and blocked drains, with the date of these blocked drains varying, it was considered that using one calibration curve for all sites would undermine these differences.



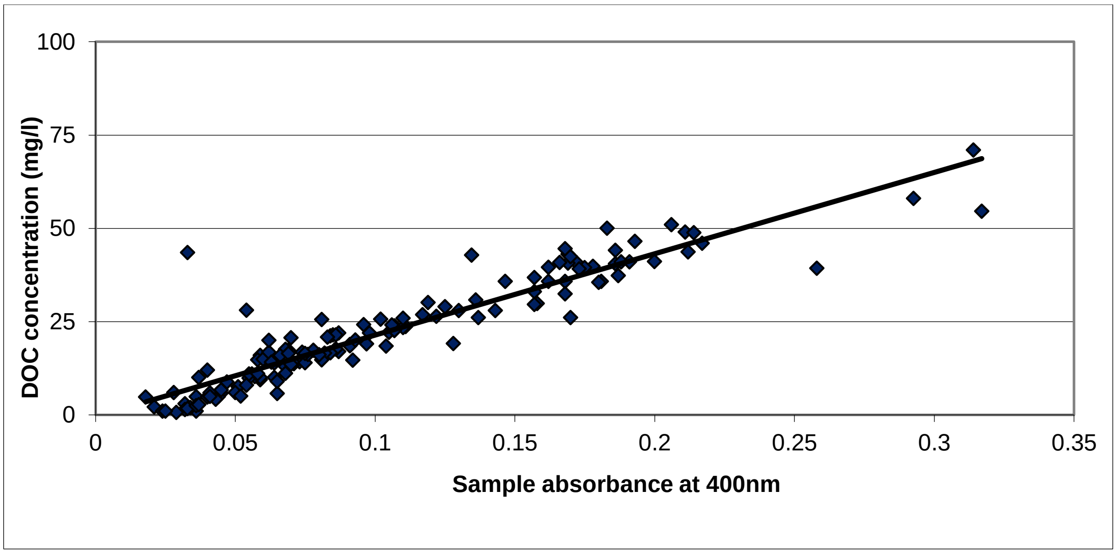
$$\text{DOC (mg/L)} = 241\text{Abs}_{400} - 0.15\ (R^2 = 0.91,\ n{=}149)$$

FIG 2.7: Calibration curve for CR1.



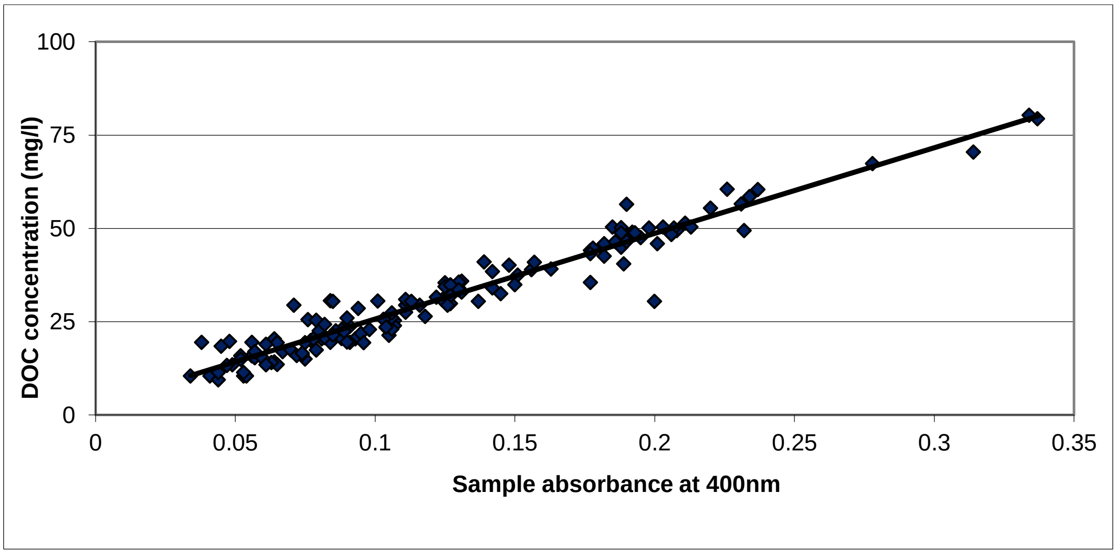
$$\text{DOC (mg/L)} = 236.23\text{Abs}_{400} - 2.51\ (R^2 = 0.88,\ n{=}150)$$

FIG 2.8: Calibration curve for CR2.



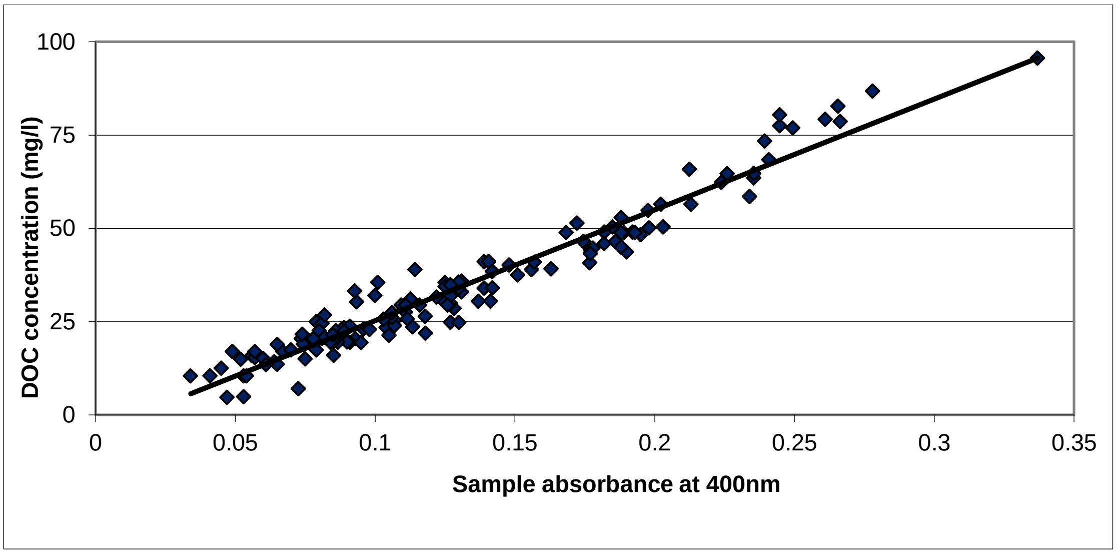
$$\text{DOC (mg/L)} = 217.86\text{Abs}_{400} - 0.39 \ (R^2 = 0.86, n=150)$$

FIG 2.9: Calibration curve for CR3.



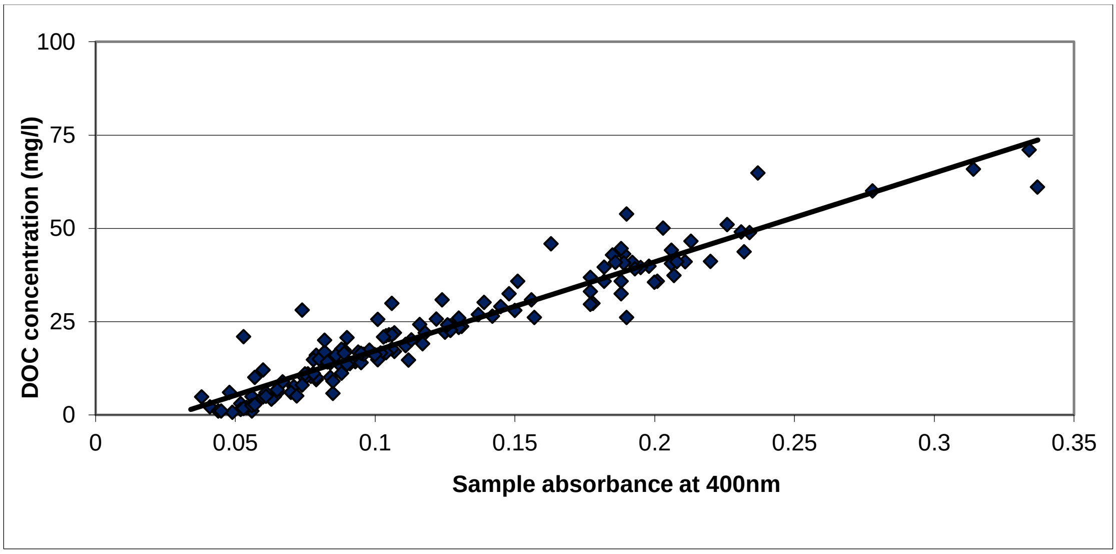
$$\text{DOC (mg/L)} = 250.02\text{Abs}_{400} - 0.07 \ (R^2 = 0.94, n=150)$$

FIG 2.10: Calibration curve for CR4.



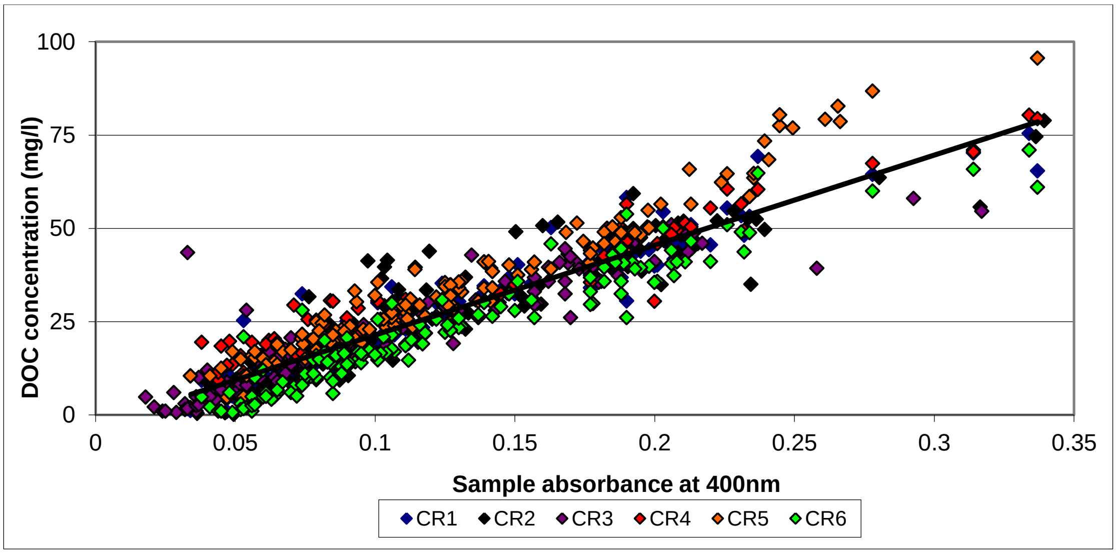
$$DOC\ (mg/L) = 260.9Abs_{400} - 1.3\ (R^2 = 0.90, n=150)$$

FIG 2.11: Calibration curve for CR5.



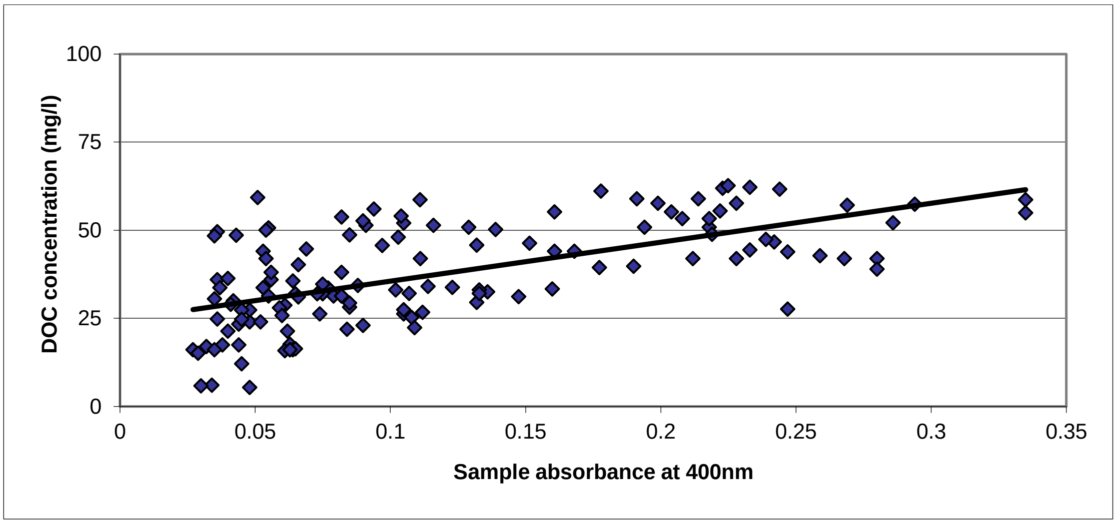
$$DOC\ (mg/L) = 242.58Abs_{400} - 0.07\ (R^2 = 0.86, n=150)$$

FIG 2.12: Calibration curve for CR6.



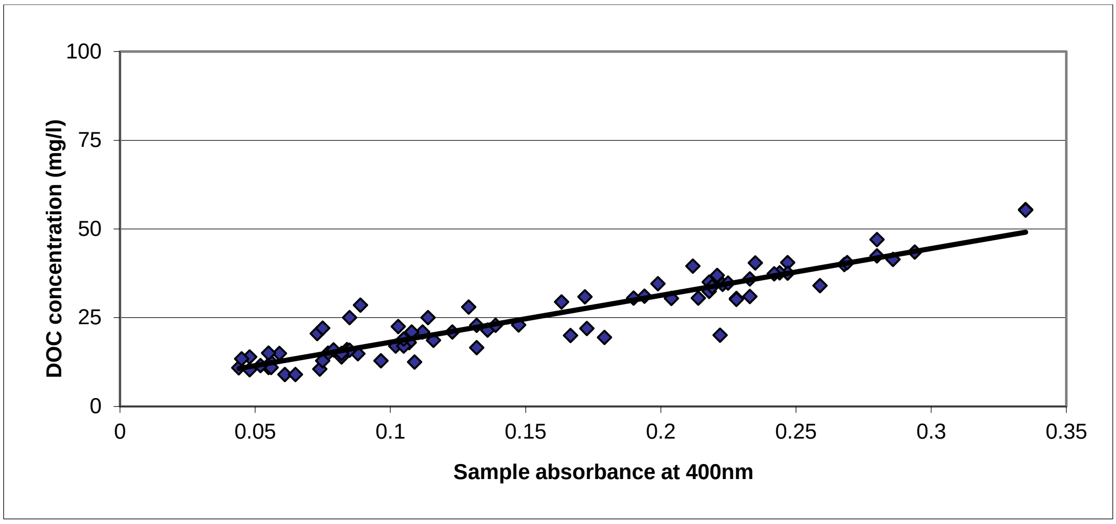
$$DOC\ (mg/L) = 201.41Abs_{400} - 0.21\ (R^2 = 0.79, n=899)$$

FIG 2.13: Combined DOC calibration curve for all sites on Cronkley Fell



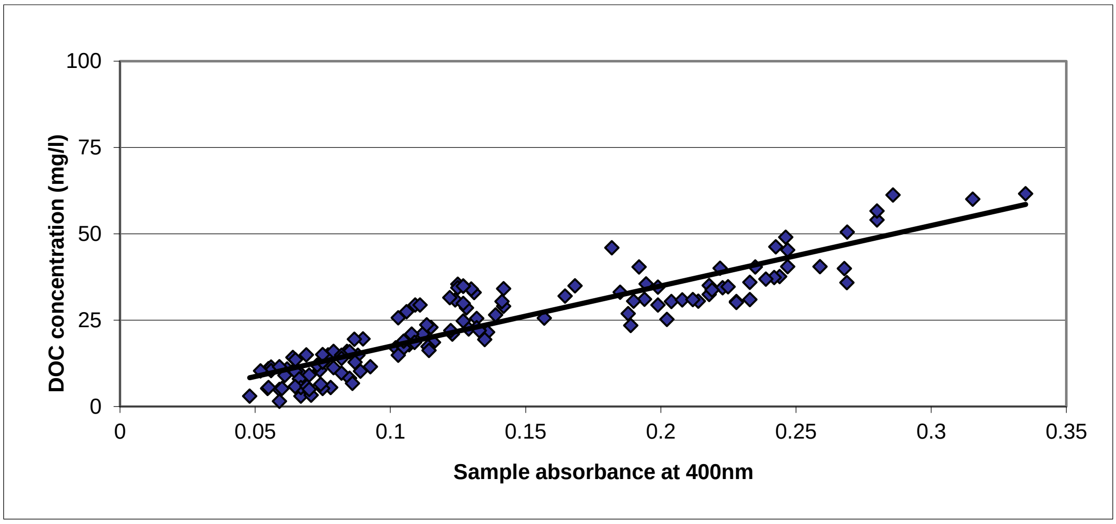
$$DOC\ (mg/L) = 199.9Abs_{400} - 0.05\ (R^2 = 0.80, n=150)$$

FIG 2.14: Calibration curve for Atkinson Moss.



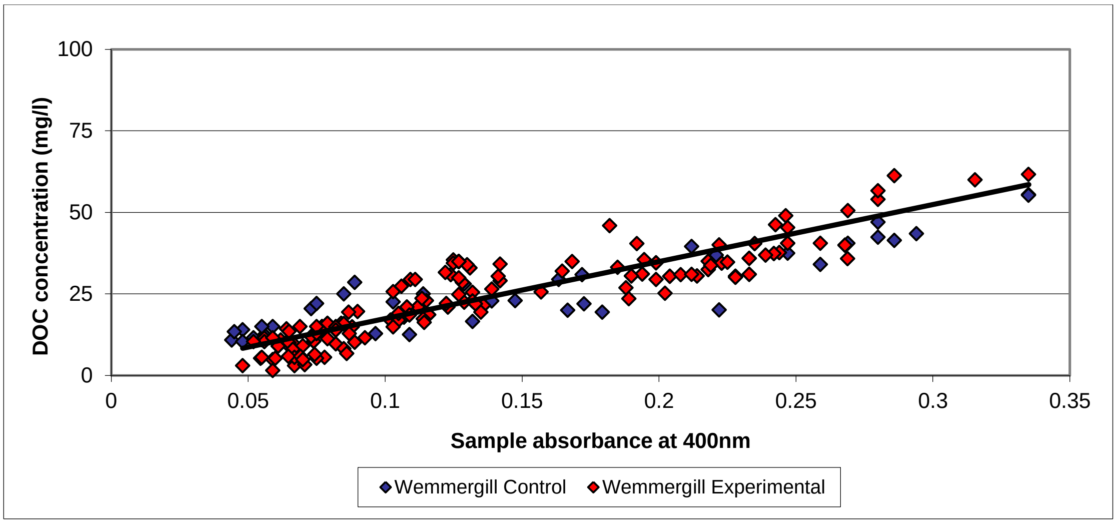
$$\text{DOC (mg/L)} = 291.54\text{Abs}_{400} - 5.55 \ (R^2 = 0.93, n=150)$$

FIG 2.15: Calibration curve for Wemmergill control.



$$\text{DOC (mg/L)} = 297.04\text{Abs}_{400} - 4.41 \ (R^2 = 0.94, n=150)$$

FIG 2.16: Calibration curve for Wemmergill experimental.



$$\text{DOC (mg/L)} = 295.38\text{Abs}_{400} - 4.82\ (R^2 = 0.81, n{=}300)$$

FIG 2.17: Combined DOC calibration curve for all sites on Wemmergill.

The calibration curves above were used to calculate DOC content for all samples from the correct 400nm absorbance measurements.

2.9.2 DOC concentration

Box plots of DOC concentration from the sites on Wemmergill (Fig 2.18) show a similar distribution of data for both the blocked experimental drain and unblocked control indicating that blocking appears to have had no effect on the concentration of DOC measured in the drains.

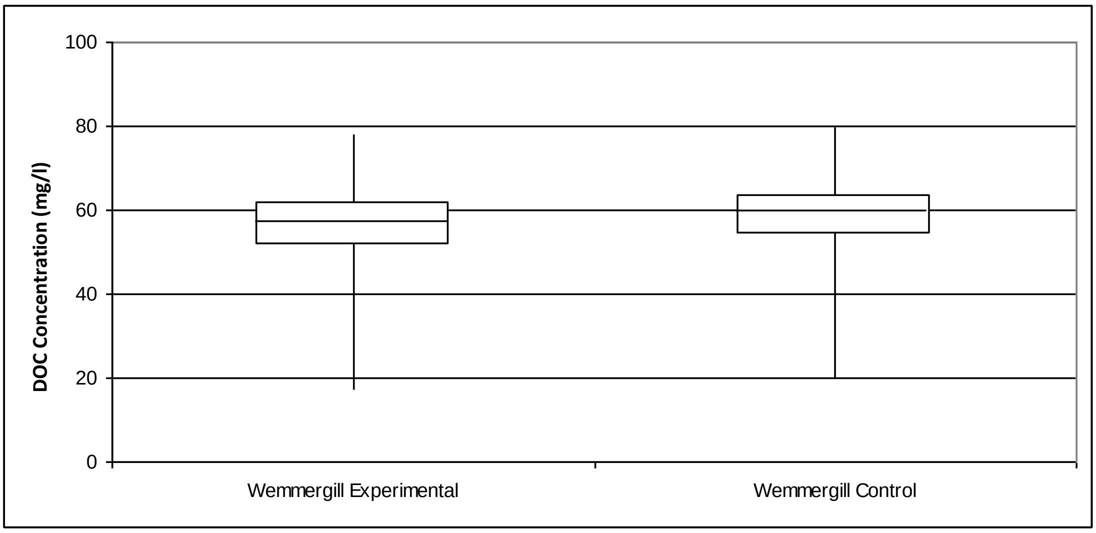


FIG 2.18: Box plot of DOC concentration for the individual drains on Wemmergill. Wemmergill Experimental, n= 691, Wemmergill Control n=804

Although the results found at Wemmergill agree with those of Gibson et al. (2009), conclusions that can be drawn from the Wemmergill data are limited. No pre-blocking data exists for the experimental drain meaning that any difference or similarities between the experimental and control drains can be explained by external parameters such as drain location and slope. The drains are located over 1 mile apart and natural variations in the peat are likely to occur in this distance thus effecting the DOC concentration recorded in any drains. Also the aim of this experiment is to consider whether the effects of blocking on an individual drain can be transferred to larger catchment scales. At the Wemmergill site only individual drains are considered meaning that although the data is useful as a comparison of what has been found in previous studies and other zero drains in this study, it does not help to shed light on the overall aim of the experiment. As such the majority of the following analysis will focus on the data collected from Cronkley Fell and Atkinson Moss.

For the control catchment on Cronkley Fell a change in DOC concentration can be observed moving upscale (CR1, CR2 – zero-order catchment, CR3 – first-order catchment, Fig 2.19) with an obvious decrease in median DOC being recorded between the zero and first order drains (Fig 2.19). This decrease is likely to be due to a combination of processes. Firstly, DOC will degrade naturally as it moves down the catchment. Experiments investigating DOC degradation have been run in tandem with this monitoring, however its influence, although statistically significant, is small and could not solely explain the decrease in DOC observed (chapter 3). Secondly, the effect of dilution at this scale is greater as an increasingly large amount of water from external sources, e.g. from soil water and soil pipes, is being added to the system. This could, in combination with degradation, cause the reduction in DOC concentration observed. In addition at larger scales the chance of stream flow interacting with mineral stream beds is increased, reducing the proportion of organic material in the stream.

The DOC concentration recorded at the pristine catchment at Atkinson Moss is significantly lower than the concentration recorded at the zero order drains at Cronkley Fell (Fig 2.19). The range of values at the pristine catchment shows a similar distribution to those recorded at the first order drain scale on Cronkley Fell where the combined effects of DOC degradation and dilution are occurring.

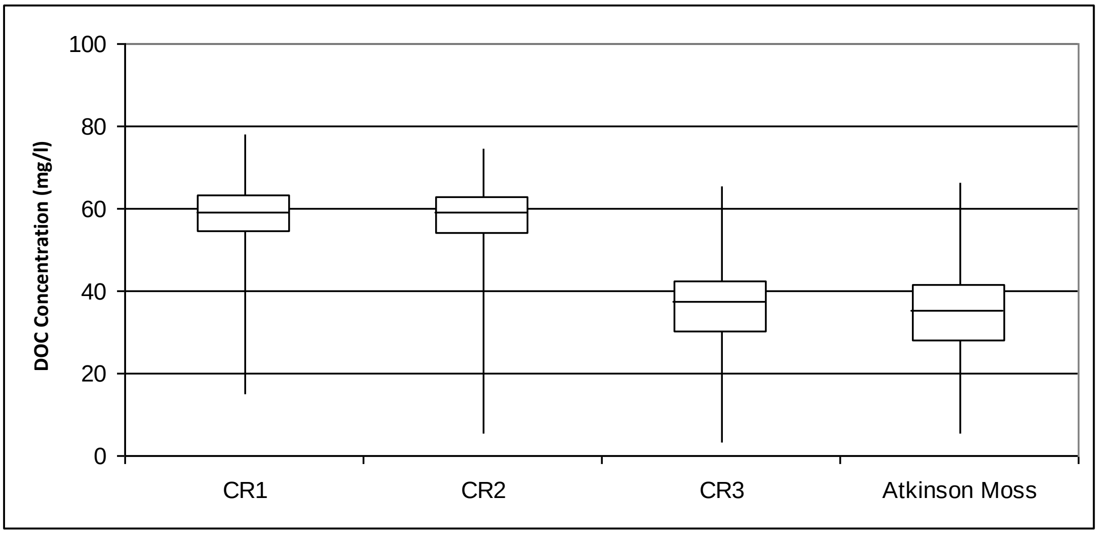


FIGURE 2.19: Box-Whisker plots of DOC Concentration for the unblocked control catchment on Cronkley Fell and the pristine catchment on Atkinson Moss. CR1 and CR2 are zero order drains on Cronkley Fell and CR3 is first order. CR1, n=1050; CR2, n=1123; CR3, n=1073; Atkinson Moss, n=2101.

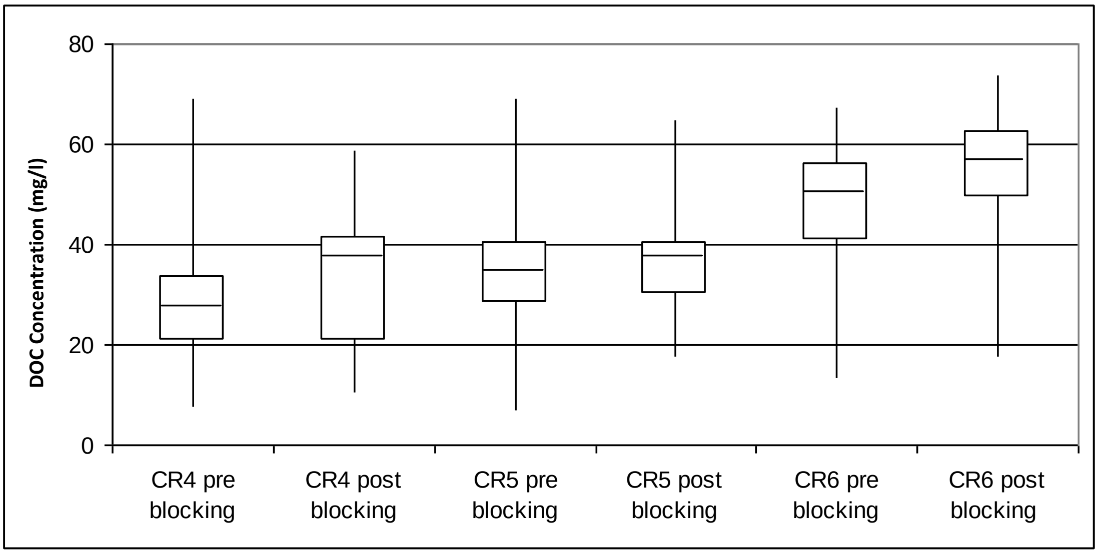


FIGURE 2.20: Box-Whisker plots of DOC concentration for the experimental catchment on Cronkley Fell in both the pre-blocking and post blocking period. CR5 and CR6 are zero order drains and CR4 is a first order drain. CR4 pre, n= 554; CR4 post, n=532; CR5 pre, n=582; CR5 post, n=548; CR6 pre, n=521; CR6 post, n=561.

The DOC concentration for the experimental catchment on Cronkley Fell (Figure 2.20) again shows a decrease with increasing scale indicating the effects of dilution and DOC degradation (CR5 and CR6 are zero order in comparison to CR4, first order). The comparison of concentration for the pre and post blocking data on the same individual drains however shows a slight increase in the drains after drain-blocking. The median DOC concentration changes upon blocking were increases of between 3% and 23%. These observed increases are likely to be an effect of the periods of monitoring: concentrations will naturally vary from year to year with increases and decreases in DOC concentration being recorded independent of blocking status.

Factor	P	Proportion of variance (%)
Site	<0.001	43.1
Month	<0.001	12.1
Site x Month	<0.001	16.2
Blocking	>0.5	
Blocking x Site	>0.5	
Blocking x Month	>0.5	
Error		28.6

Table 2.1: ANOVA of DOC concentration for all monitored sites and months giving the probability of the factor/interaction and the proportion of the variance explained by the factor.

ANOVA was performed on the DOC concentration data from Cronkley and Atkinson Moss and it was found that site, month of the year and the interaction between site and month are significant factors at the 95% probability (Table 2.1). The site factor explains the majority of the variance in the dataset but the error term still explains 28.6% of the variance of the DOC concentration. It should be stressed here that the error term in ANOVA represents the unexplained variance and is not just a matter of sampling or measurement error. It could, for example, represent factor interactions that could not be estimated here. The site factor shows co-linearity with scale and the site factor's significance in the ANOVA analysis reflects the reduction in DOC concentration observed at increasing scale shown in figures 2.19 and 2.20. Site was used as a factor in the ANOVA rather than scale in order to include the DOC concentration from the pristine catchment at Atkinson Moss where monitoring occurs on a natural stream which cannot be accurately categorized as either a zero or first order drain. The blocking status of the drain was found not to be a significant factor in explaining the variance of the DOC concentration record confirming which was inferred from the box-whisker plots above (Figures 2.19 and 2.20). The presence of a significant interaction between site and month suggests that the different sites have different seasonal cycles. This is unlikely to be the case between the control and experimental catchments on Cronkley Fell due to their close proximity. The significant interaction is more likely to reflect a different seasonal cycle between both sites on Cronkley Fell and Atkinson Moss.

2.9.3 Relative DOC concentration

To negate any effects of the natural variation in DOC from year to year the DOC concentration of a blocked drain should be considered relative to the DOC concentration of an unblocked drain of the same scale in the control catchment. Relative DOC is calculated by the ratio of the monthly average DOC concentration of a blocked and unblocked drain from the experimental and control catchment respectively.

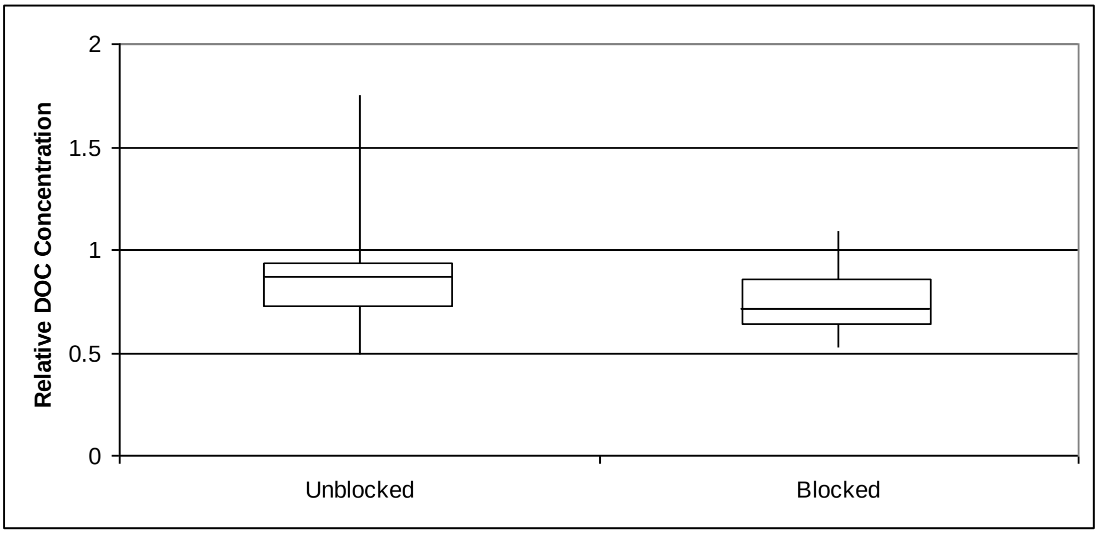


FIGURE 2.21: Box plots of relative DOC concentration at the first order scale for the blocked and unblocked period in the experimental catchment relative to the control catchment on Cronkley Fell.

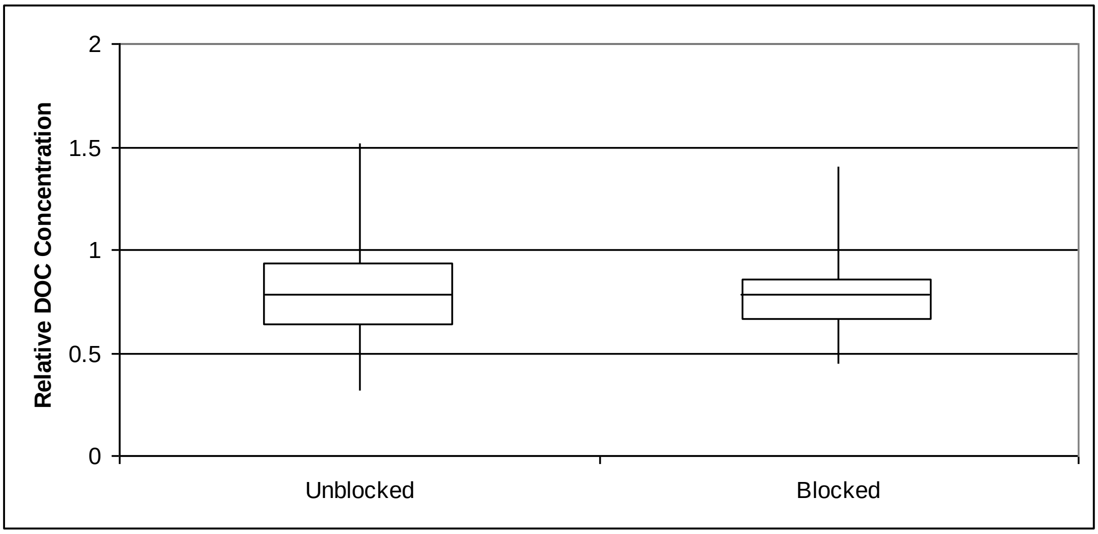


FIGURE 2.22: Box plots of relative DOC concentration at the zero order scale for the blocked and unblocked period in the experimental catchment relative to the control catchment on Cronkley Fell.

The comparison of the relative DOC concentration (Figures 2.21 and 2.22) shows that at all scales the experimental catchment has a lower relative DOC concentration than the control, i.e. relative concentration medians are less than 1. At the first order scale drain-blocking also appears to have suppressed the range of relative DOC concentrations compared to the drained catchment. When the relative DOC concentrations for blocked and unblocked drains are compared (Figure 2.21) a small yet statistically significant reduction can be observed at the first order drain scale – the reduction is approximately 2.5%. The relative DOC concentration for unblocked and blocked drains at the zero order scale (Figure 2.22) shows a decrease post blocking; however this is not statistically significant.

Factor	P	Proportion of variance (%)
Month	<0.001	22.2
Scale	<0.001	18.6
Blocking	<0.001	6.9
Blocking x Scale	<0.001	2.9
Scale x Month	>0.5	
Blocking x Month	>0.5	
Error		49.4

Table 2.2: ANOVA of relative DOC concentration for all monitored sites and months giving the probability of the factor/interaction and the proportion of the variance explained by the factor.

ANOVA was performed on the relative DOC concentration factor and it was found that scale, month of the year, blocking and the interaction between blocking and scale are significant factors at the 95% probability (Table 2.2). The month factor explains the majority of the variance in the dataset reflecting the seasonal trends in the DOC record but the error term still explains 49.4% of the variance of the DOC concentration. In contrast to the DOC concentration analysis blocking is found to have a small yet still statistically significant effect on relative DOC concentration. Along with the significance of scale this suggests that compared to the control catchment blocking may be having an effect on DOC concentration as scale changes. The significance of blocking status, scale and their interaction reflects a significant decrease in relative DOC concentration recorded post blocking at the first order scale which is not recorded at the zero order scale (Figures 2.21 and 2.22). The average size of this decrease was calculated above as 2.5% relative to the control catchment at the first order scale.

2.9.4 DOC Export

The export of DOC is a measure of the amount of DOC leaving the study catchments per unit area. Annual and monthly DOC exports have been calculated for the period from August 2007 to April 2010 for all monitored localities. Analysis of the monthly time series (Appendix 8.2, Fig. 2.23, 2.24 and Fig. 2.25) for all the monitored sites shows strong seasonal cycles with increases in DOC export being observed during the spring and autumn flush.

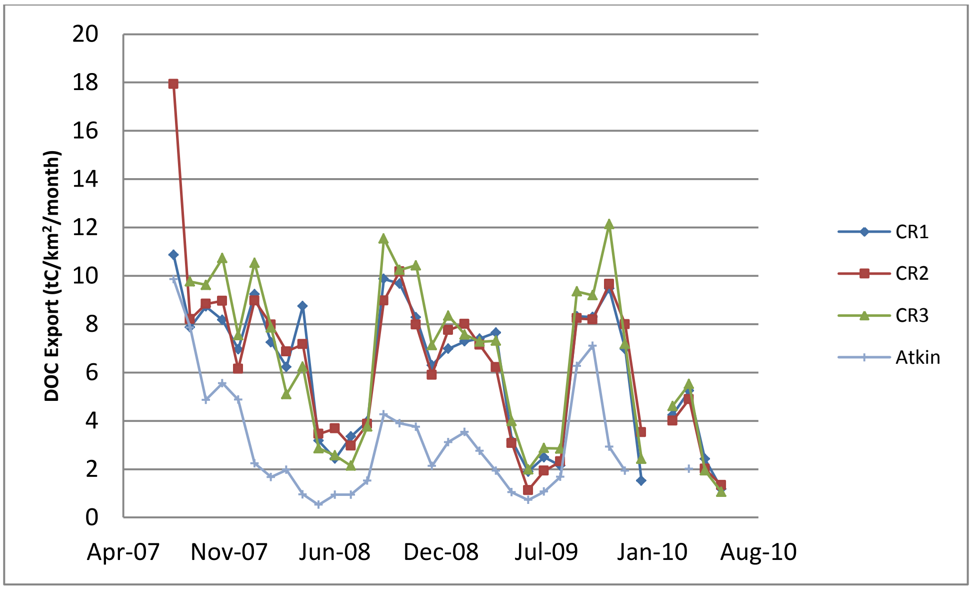


FIG 2.23: Monthly DOC export time series for the control catchment on Cronkley Fell and Atkinson Moss.

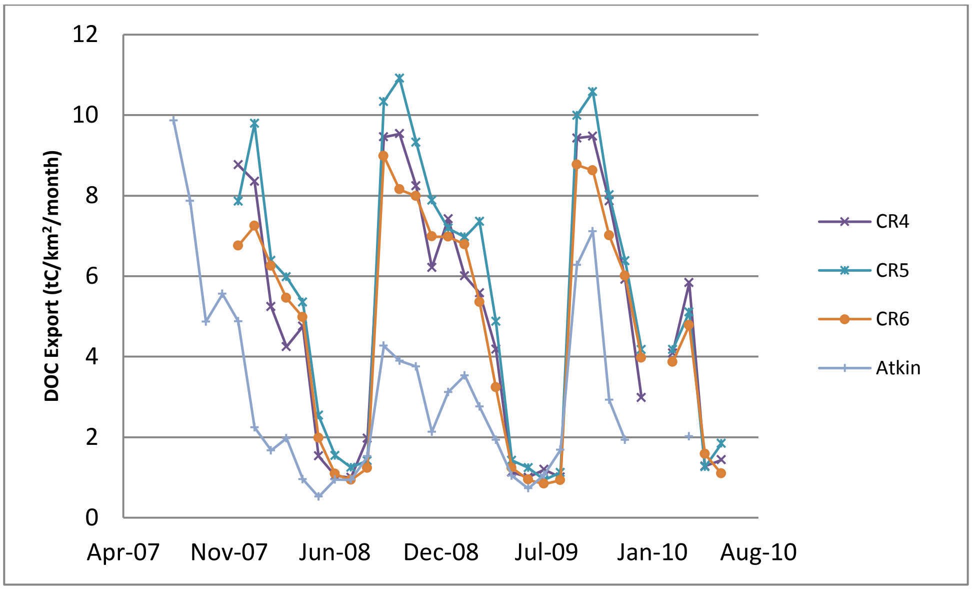


FIG 2.24: Monthly DOC export time series for the experimental catchment on Cronkley Fell and Atkinson Moss.

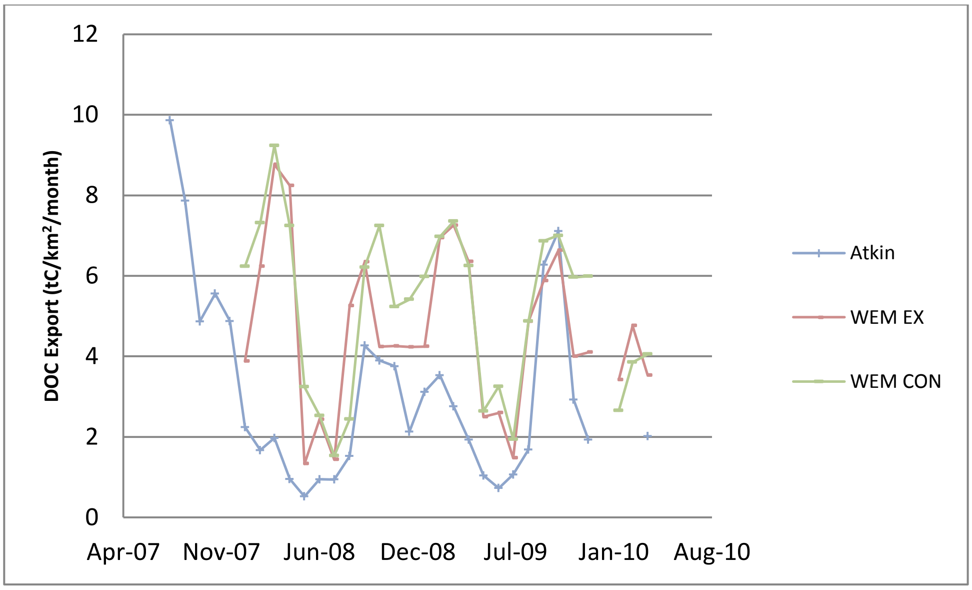


FIG 2.25: Monthly DOC export time series for Wemmergill and Atkinson Moss.

Values for total annual DOC export vary with the smallest export being recorded at the pristine catchment at Atkinson Moss and the highest value being recorded at the first order drain scale on Cronkley Fell (Table 2.3). A reduction in annual DOC export from the pre to post blocking period is recorded for all sites on Cronkley Fell. However, the size of this reduction varies depending on catchment and scale. A reduction of approximately 1.7% is recorded for the zero order drains on the control catchment and 0.45% for the first order drain. This reduction reflects the natural year on year variation of DOC export. However, the reductions recorded at the experimental catchment are larger with an approximate 9.2% reduction in DOC export at the zero scale and 2.2% reduction at the first order. These reductions at the experimental catchment reflect the combined effects of natural year on year variation and the effects of blocking on DOC export. The data from the Wemmergill sites indicates that there is little change year on year but an approximate 12% reduction in annual DOC export is recorded when the blocked drain is compared to the unblocked control.

Site	Catchment/Scale	Total DOC Export Pre-blocking year (tC/km^2)	Total DOC Export Post-blocking year (tC/km^2)	% Change in DOC Export
CR1	Control zero-order	78.54	77.10	-1.83
CR2	Control zero-order	77.97	76.65	-1.68
CR3	Control first-order	80.44	80.07	-0.45
CR4	Experimental first-order	61.57	60.20	-2.21
CR5	Experimental zero-order	72.70	66.07	-9.11
CR6	Experimental zero-order	62.56	56.70	-9.35
Atkinson Moss	Pristine	24.83	34.09	14.26
Wemmergill Experimental	Blocked zero-order	56.65	56.84	0.03
Wemmergill Control	Unblocked zero-order	63.87	65.96	1.9

Table 2.3: Annual total DOC export values

ANOVA was performed on the monthly DOC export data and it was found that when water yield is included in the analysis as a covariate, water yield, site, month of the year, blocking status and the interaction of blocking and site are all significant at the 95% probability (Table 2.4). The water yield factor explains the majority of the variance in the dataset but the error term still explains 24.2% of the variance of the DOC export. When water yield is excluded as a covariate from the analysis, site, month of the year, blocking status and the interaction of blocking and site are found to be significant (Table 2.4) with the majority of the variance being explained by site and an increased importance of the error term of 32.9%. The sites factor's significance in the ANOVA reflects the changes in DOC export observed as scale increases. The significance of site, blocking status and the interaction between the two reflects the decrease in DOC export recorded post blocking in the experimental catchment and how the size of this reduction decreases from zero to first order drain. The blocking of the drains caused an obvious decrease in water yield through the drain as the water is held back in the peat. This leads to less flushing of the DOC through the drain thus a lower recorded DOC export. At larger scales this effect of blocking on DOC export is reduced indicating that although the drain blocks at this scale are causing a decrease in water yield, additional water is being added to the system via bypass flow and external spatially variable sources suppressing the DOC export reduction.

Factor	P	Proportion of variance (%) with Water Yield	Proportion of variance (%) without Water Yield
Water Yield	<0.001	29.4	
Site	<0.001	18.5	25.8
Month	<0.001	14.3	18.2
Blocking	<0.001	7.9	12.6
Blocking x Site	<0.001	5.7	10.5
Blocking x Month	>0.5		
Site x Month	>0.5		
Error		24.2	32.9

Table 2.4 ANOVA of DOC Export for all monitored sites and months giving the probability of the factor/interaction and the proportion of the variance explained by the factor.

A linear relationship is observed between water yield and DOC export for all zero order monitored localities indicating that the reductions in DOC export observed post blocking can be explained by a decrease in water yield rather than concentration. A plot of DOC export against water yield for the zero order sites in the experimental catchment at Cronkley Fell and Atkinson Moss (Figure 2.26) demonstrates how blocking causes data points to move down a linear trend line as water yield is increasingly held back by blocking until the drain demonstrates the characteristics of the undrained catchment at Atkinson Moss. At the first order scale a linear trend is still recorded between water yield and DOC export (Figure 2.27), however this trend is less well defined with analysis of the trend indicating a reduced R^2 value. DOC export post blocking was seen to reduce however this reduction was observed to decrease with increasing scale with zero order drains showing a 9.2% reduction in annual DOC export and the first order drain showing only a 2.21% decrease. There are several possible causes for this. Bypass flow around the zero order blockages may be adding additional water to the first order drains suppressing the impact of the export reduction at this scale. The mixing of water from bypass flow or any dilution effects from alternative sources of water would disrupt the well-defined linear relationship between water yield and DOC export creating the more diffuse pattern of data seen in Figure 2.27. Also the combined effects of DOC degradation may be acting at this larger scale. The presence of any component of bypass flow or external water sources will reduce the efficiency of any blocking.

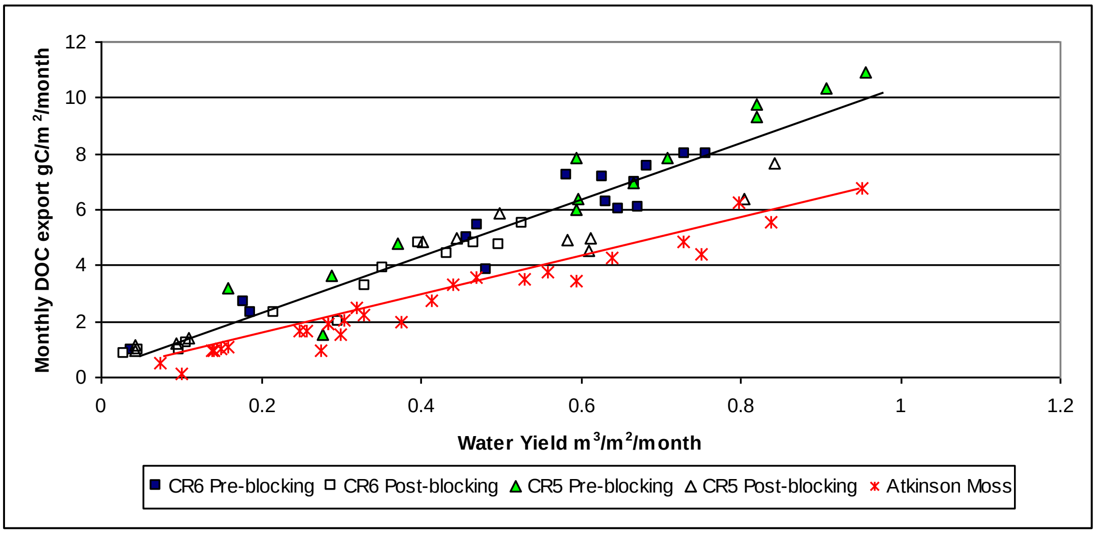


FIGURE 2.26: The correlation between water yield on DOC export at the zero order scale for the experimental catchment at Cronkley Fell and Atkinson Moss. Cronkley zero order trend line: y=17.85x + 1.02, R^2=0.83; Atkinson Moss trend line y=10.72x + 0.91, R^2= 0.87.

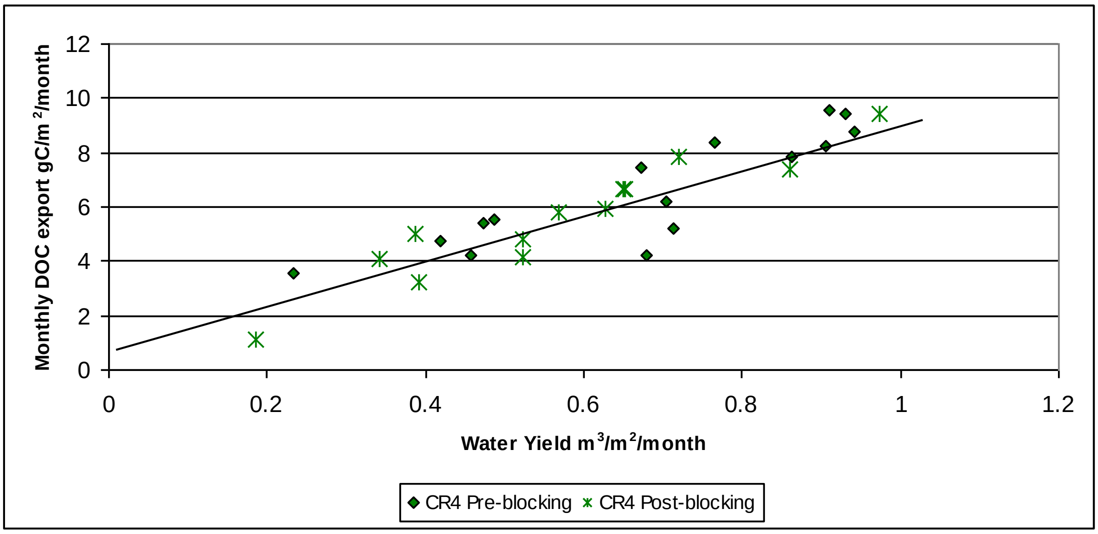


FIGURE 2.27: The correlation between water yield and DOC export for the first order drain on the experimental catchment of Cronkley Fell. Trend line, y=15.33x + 0.62, R^2=0.71

2.9.5 Relative DOC Export

In the same way that relative DOC concentration was calculated, the relative DOC export was calculated between the blocked and unblocked drains in order to negate any effects of the natural variation in DOC concentration and water yield from year to year. Relative DOC export was calculated by the ratio of the monthly average DOC export of a blocked and unblocked drain from the experimental and control catchment respectively.

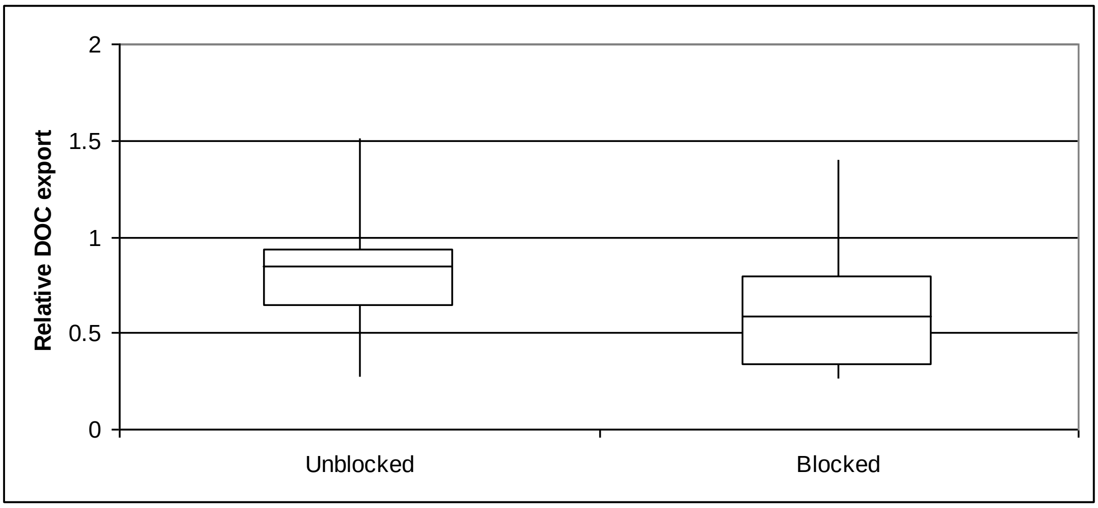


FIGURE 2.28: Box plots of relative DOC export at the zero order scale for the experimental catchment relative to the control for the blocked and unblocked period on Cronkley Fell.

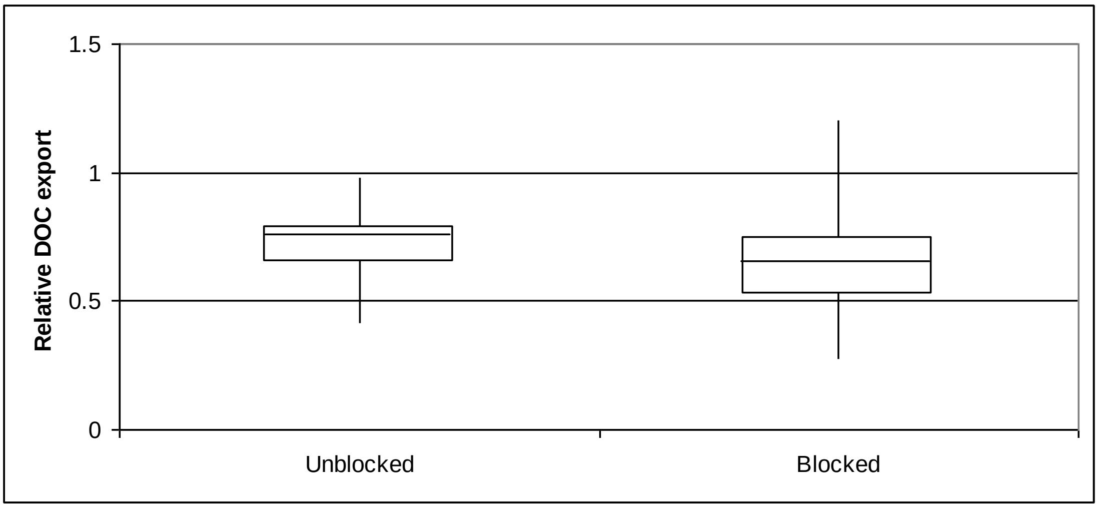


FIGURE 2.29: Box plots of relative DOC export at the first order scale for the experimental catchment relative to the control for the blocked and unblocked period on Cronkley Fell.

The comparison of the relative DOC export (Figures 2.28 and 2.29) shows that at all scales the experimental catchment has a lower relative DOC export than the control, i.e. relative export medians are less than 1. A statistically significant reduction in relative DOC export is recorded between the blocked and unblocked drains at both scales however this reduction is smaller at the first order scale with a 7.3% reduction on the zero order drains and a 1.8% reduction at the first order drains.

Comparison of the datasets indicates that blocking appears to increases the range of relative DOC export vales at both scales.

ANOVA was performed on the relative DOC export data and it was found that water yield, month of the year, scale, blocking and the interaction between blocking and scale are significant factors at the 95% probability (Table 2.5). The error term explains 39.2% of the variance. Similarly to the DOC export the water yield factor explains the majority of the variance in the relative DOC export dataset. This indicates how those decreases in DOC export recorded post blocking are controlled by a reduction in water yield rather than DOC concentration although a small reduction in relative DOC concentration, approximately 2.5% was record at the first order drain scale. The significance of scale, blocking status and their interaction reflects again how the reduction in DOC export post blocking is seen to diminish as scale increases. This is indicative of the effects of bypass flow around the blockages at the zero order scale adding additional water at the first order. This leads to a higher water yield at the first order scale thus the reduction in DOC export caused by the blocking at this larger scale is smaller.

Factor	P	Proportion of variance (%)
Water Yield	<0.001	17.8
Month	<0.001	16.2
Scale	<0.001	15.9
Blocking	<0.001	6.8
Blocking x scale	<0.001	4.1
Blocking x month	>0.5	
Scale x month	>0.5	
Error		39.2

Table 2.5: ANOVA of relative DOC export for all monitored sites and months giving the probability of the factor/interaction and the proportion of the variance explained by the factor.

2.9.6 Double mass analysis

A linear trend has been demonstrated between DOC export and water yield for zero order drains (Figure 2.26). Double mass curves were created for the cumulative monthly DOC flux against water flux for drains in the control and experimental catchment on Cronkley Fell to examine whether blocking can be seen to affect this linear trend and whether any effect would be visible at a larger first order scale.

A change in the slope of the double mass curve is observed in the month post blocking for the zero order drains (CR5, CR6) on the Cronkley Experimental catchment (Figure 2.30). This indicates that a change in the DOC regime has occurred post blocking. However, this change in DOC regime is not visible on the first order drain (CR4). The trend continues in a linear fashion similar to those seen on the double mass curve for the control catchment where no drain blocking has occurred (Figure 2.31). A lack of slope break for the control catchments excludes the possibility that the break in slope observed for experimental catchment is due to a common change for both catchments.

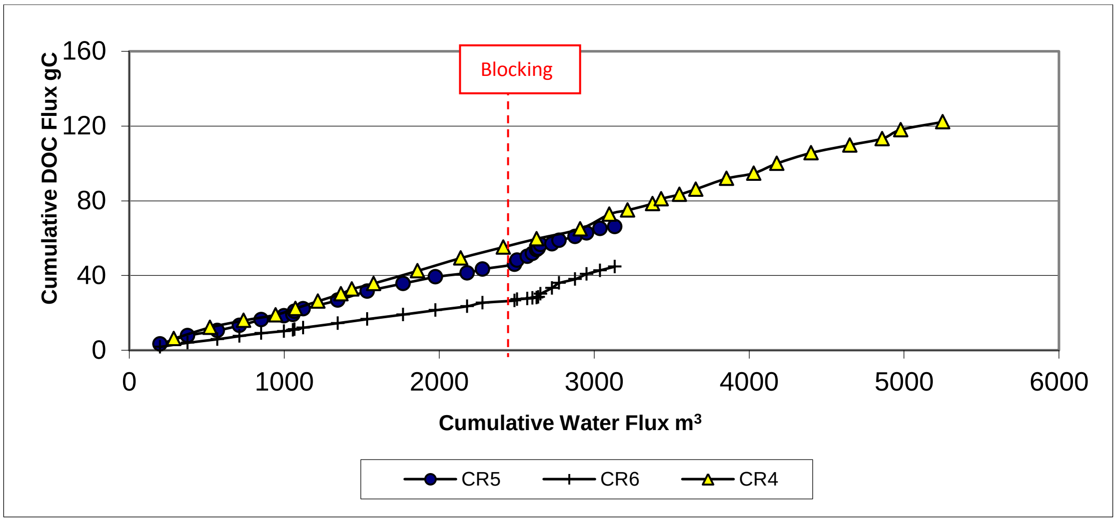


FIGURE 2.30: Double Mass Curve for the Cronkley Experimental catchment. The data points represent cumulative monthly intervals.

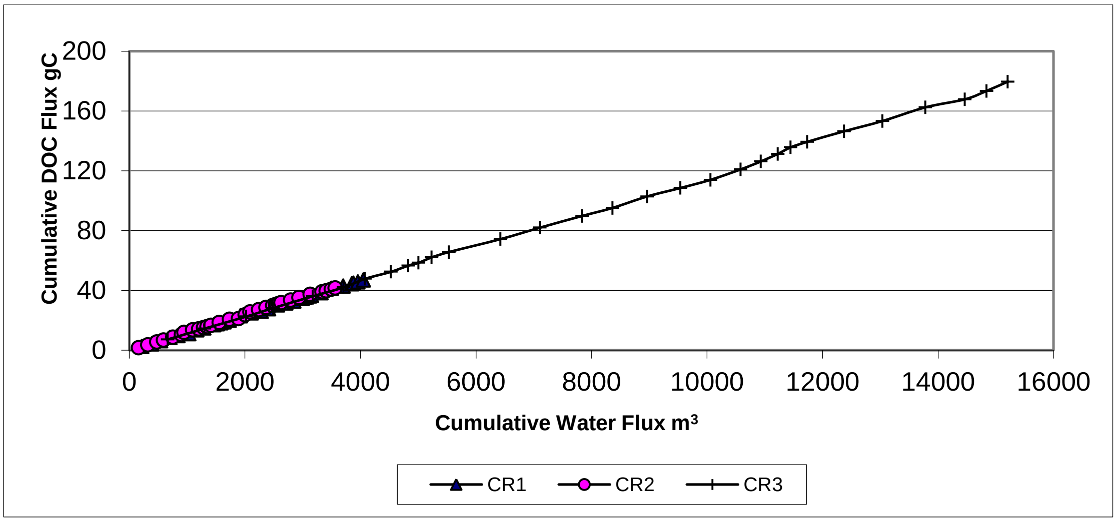


FIGURE 2.31: Double Mass Curve for the control catchments on Cronkley Fell. The data points represent cumulative monthly intervals.

The double mass analysis also shows other small changes in slope which can be attributed to natural seasonal changes in DOC export. Seasonal cycles are visible on all double mass curves during the summer months when less water is flowing in the drains thus less DOC is being exported from the area. The seasonal effect on cumulative DOC flux can be seen in Figures 2.32 and 2.33 for the experimental and control catchment. The change in slope indicated on the zero order drains in Figure 2.30 in the month post blocking is cannot be matched with any seasonal change in slope indicated on Figures 2.32 and 2.33. This indicates that the change in slope on Figure 2.30 is indeed an effect of a change in DOC regime post blocking.

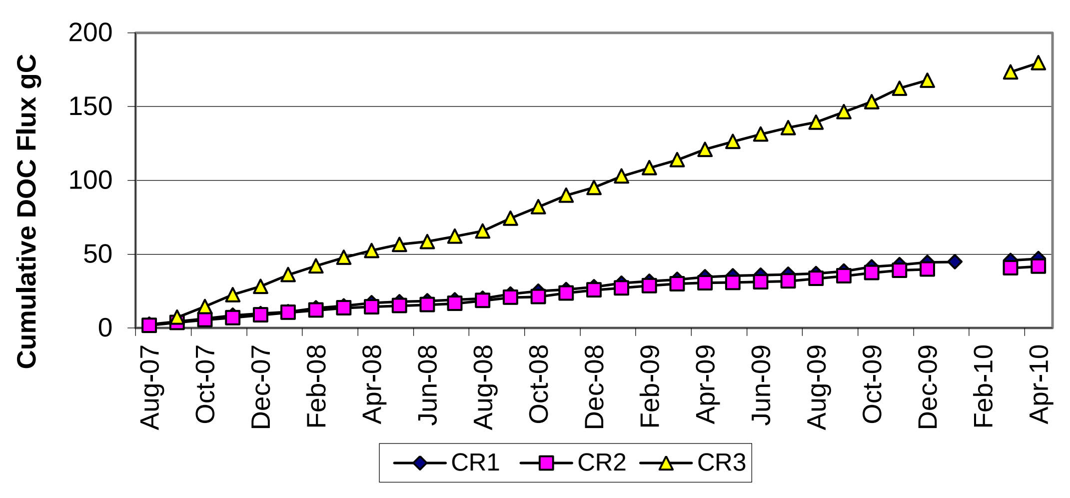


FIGURE 2.32: The seasonal effect on cumulative DOC Flux in the control catchment. The data points represent cumulative monthly intervals.

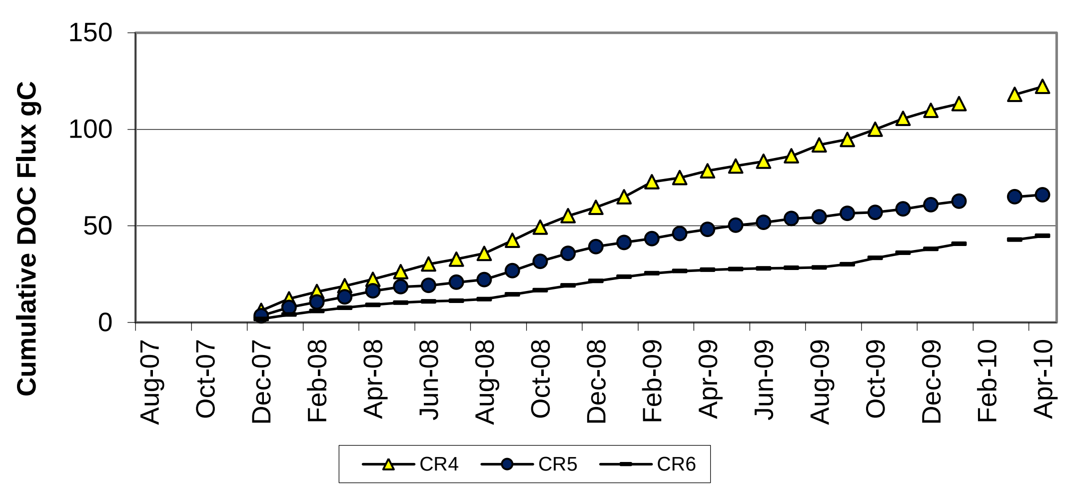


FIGURE 2.33: The seasonal effect on cumulative DOC Flux in the experimental catchment. The data points represent cumulative monthly intervals.

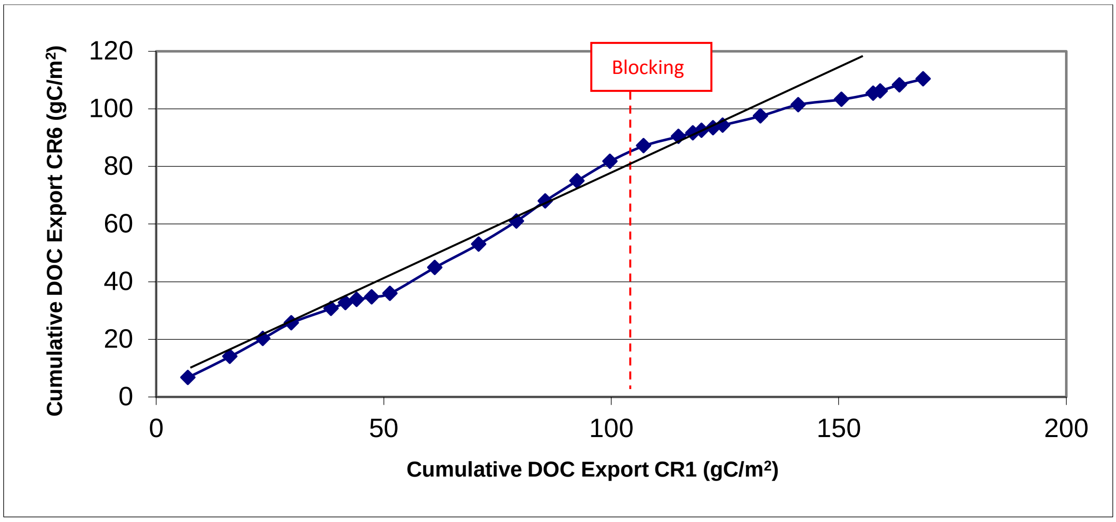


FIGURE 2.34 Double mass curve for DOC export for a zero order drain in the control and experimental catchments on Cronkley Fell. CR1, control catchment; CR6, experimental catchment. The black trend line indicates the straight linear trend from which the curve is tending away. The data points represent cumulative monthly intervals.

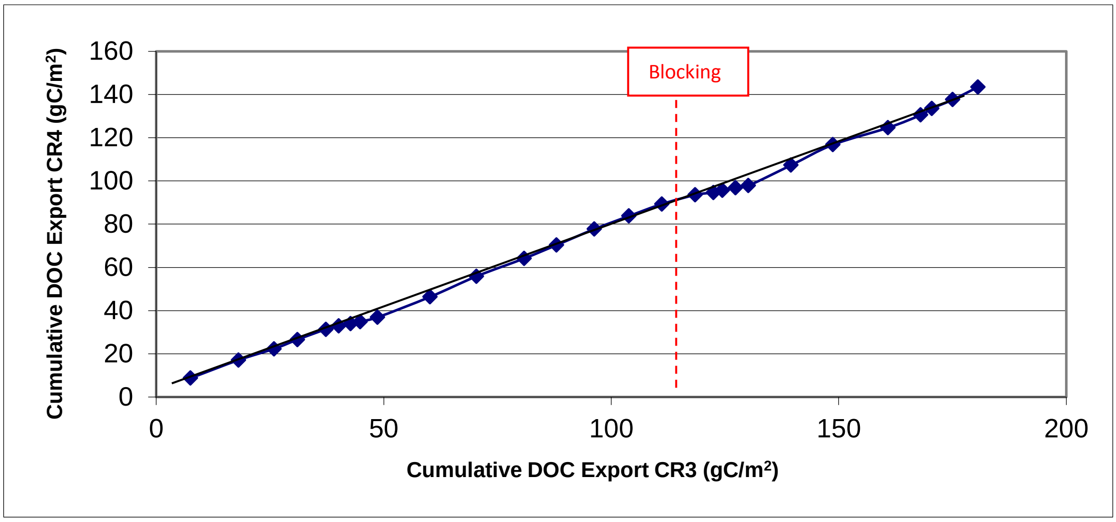


FIGURE 2.35: Double mass curve for DOC export for a first order drain in the control and experimental catchments on Cronkley Fell. CR3, control catchment; CR4, experimental catchment. The curve does not tend away from the trend line post blocking. The data points represent cumulative monthly intervals.

The change in the DOC regime post blocking can furthermore be observed relative to the same scale drain in the control catchment. Double mass curves of DOC export of a zero order drain in the experimental catchment and a zero order drain in the control catchment (Figure 2.34) indicate a change in slope, in the period post blocking, indicating a change in trend between the two drains with DOC export accumulating more rapidly on the unblocked drain. No obvious change in trend is again visible when a similar process is applied to the first order drains (Figure 2.35), with the first order drain in the experimental catchment continuing to follow a similar trend to that in the control catchment post blocking.

2.10 Discussion

So can this study demonstrate that drain-blocking significantly reduces DOC concentrations in surface waters? The detail of this study in being able to report a drain-blocking experiment with a paired catchment approach with both pre- and parallel controls at multiple scales means it is possible to shed light on previous studies. Firstly, if it had only been possible to measure after drain blocking and compare it to an open drain this study would have concluded that for first-order streams drain blocking would increase DOC concentrations. With respect to DOC export, if the blocked drain was compared to its neighbouring unblocked drain, the effect of blocking would have been estimated at 24% reduction for the zero order drains and 12% reduction in DOC export for the first order drains, than that of the open drains. However it would not be clear from the data how much of this reduction in DOC export is due to the blocking and how much is due to the natural hydrological variations between the two monitored catchments. Being able to monitor prior to blocking allows a baseline for both the water yield and water colour to be established so that the size of the influence of blocking can be correctly assessed. Thus a reduced value for the effect of blocking on DOC export can be established at 9.2% for the zero order drains and 2.2% at the first order.

Secondly, if this study could only consider the drains before and after drain-blocking without relation to a parallel control it would conclude that in the post blocking year a slight increase in DOC concentration had been recorded at both zero and first order scales. The presence of a control catchment allows this increase to be interpreted as a natural year on year variation and not any effect of blocking. Further, it should be noted that the detail of this study means that it would be possible to demonstrate significant differences in each of these two conjectured comparisons. It is only in the detail of the relative comparison before and after drain blocking that this study can conclude that there was a significant effect and that drain blocking does lower DOC concentration if only in a limited fashion. This does mean that previous studies (incl. Worrall et al., 2007a and Gibson et al., 2009) must be treated as limited if not actually misleading. Even with the more detailed analysis included in this study only a small effect of drain-blocking has been found and this decreases with scale suggesting that at larger scales the effect of blocking may be lost.

The small effect of drain-blocking upon DOC concentration is reflected in the changes in DOC export observed, i.e. the dominant affect observed is small when water yield is also considered. The export of DOC was seen to reduce at the zero order scale in a linear fashion with water yield as the blocking of drains causes the water to be held back in the peat. Thus less DOC is lost from the system. This decrease in the size of this DOC export reduction upscale gives evidence of a component of bypass flow or ‘leakage’ around the blockage at the zero order scale adding high DOC concentration water to the system down the catchment. The addition of water to the system at the first order channel scale does suggest that bypassing of drain blocks down the slope or on the highest flows is occurring which would suppress the size of the DOC export reduction at this scale. At present it is not possible to comment on the nature of the balance of flowpaths that contributing to this effect.

This study has demonstrated that a small, if significant, effect on DOC does exist for these study sites. Therefore, two questions arise – what is causing this change? and why is it not larger? The decrease in DOC concentration could be due to a balance between enzymic-latch effects, or sulphide-oxidation effects causing increases in DOC production or solubility upon the rise of the water table against reduced DOC production due to reduced depth of the aerobic zone. Both of these effects will be greater with a greater change in the depth of the water table and indeed the small magnitude of the effect observed in this study may well be explained by the fact the average change in depth to water table for the study was only 1 cm from 6cm depth to 5cm depth (chapter 4), i.e. the change in water table was very slight. Worrall et al. (in review) have shown a statistical decline in soil and runoff water DOC concentration upon cutting or burning of *Calluna vulgaris* on a peat soil and have associated this decline with change in water table depth. Lower DOC concentrations occurred as water tables became shallow, but the average change in water table depth was 40 cm.

2.11 Conclusions

This study has shown that:

1. There was no significant decline in DOC concentration at zero or first order scale post blocking; however a small yet significant decline of 2.5% in relative DOC concentration was recorded at the first order scale.
2. A decrease in DOC concentration is recorded as water flows from the zero to the first order in the same catchment indicating the importance of dilution effects in the catchments and the influence of in stream DOC loss processes such as DOC degradation.
3. The blocking of peat drains does significantly decrease the export of DOC from peat drains; however this is largely achieved by decreasing water yield.
4. The size of the DOC export reduction caused by drain blocking is seen to decrease as scale increases providing evidence for the existence of bypass flow around the zero order drain blockages.

Although drain blocking is successful in reducing DOC export at all scales this success seems to decline as scale increases with reductions in DOC export being suppressed as the catchment hydrology increase in complexity at larger scales.

3. The in-stream loss of DOC in an upland peat-covered catchment.

3.1 Introduction

In order to assess how the impact of drain blocking upon DOC concentration and flux changes with scale it is necessary to assess whether other effects could be contributing to a changes in DOC concentration that are not due to the blocking: the transition between zero- and first-order takes time and so any decline in concentration could be in-stream processing. These other effects would include the natural degradation of DOC in the stream waters and any dilution effects that would occur as the water moves upscale. These effects are important limitations on assessing the extent of any benefits of drain blocking and when considered together with the calculated DOC budgets any reduction in water colour observed post blocking may be suppressed. As scale increases the influence of in-stream factors will also increase and they must therefore be considered in any budget calculations. This chapter aims to measure in-stream processing of DOC as well as establishing the levels of dissolved carbon dioxide (CO_2) in the surface waters, i.e. the product of the degradation of DOC. The issue of water dilution and mixing is discussed in chapter 4. This study therefore considered the effects of both biochemical degradation by calculating the biochemical oxygen demand (BOD) and photodegradation by the incubation of raw water samples in uv-transparent quartz tubes. Estimations of the level of dissolved CO_2 in the surface water were based upon measured stream water acidity.

This chapter aims to investigate the influence of those effects that, independent of blocking status, increasingly affect the DOC budget as scale increases. The chapter first discusses the impact of these parameters before introducing the methods in this investigation. This is followed by the presentation of laboratory results and statistical analysis. The significance of these results is then discussed.

3.2 The loss of carbon in a peat- covered catchment

As discussed in chapter 2, peatlands contain a third of the global soil carbon (Gorham, 1991). Within the UK they represent the country's largest single terrestrial carbon store, storing more carbon than the forests of the UK and France combined and are presently assumed to be a net annual sink of carbon. Cannell et al. (1999) estimates that the annual loss of carbon from UK rivers is of the order 0.68 Mt C/yr and Aitkenhead et al. (1999) suggests that the majority of this carbon will be lost from peatlands. The fluvial flux of carbon from peatlands represents between 35 and 50% of their total carbon flux (Dawson et al., 2002).

Dawson et al. (2002) indicates that fluvial loss of carbon from upland peat covered catchments consists of the flux of DOC, particulate organic carbon (POC) and dissolved inorganic carbon (DIC) such as dissolved CO_2. Several studies have considered POC, DOC and DIC such as Schlesinger and Dawson (1981) and Meybeck et al. (1993). Meybeck et al. (1993) estimated that the flux of DOC and DIC from the World's rivers was of the order of 542 Tg C/yr. Both these studies however did not consider that any water on the surface of the earth is in contact with a CO_2 containing atmosphere and thus contains inorganic carbon by this fact. Also they did not consider the loss of carbon within the river itself leading to an underestimation of carbon loss from the catchment.

Not only is dissolved CO_2 lost in transit within the river system, DOC can be mineralised within the river system itself. A number of studies have shown that this loss in DOC can be significant. Worrall et al. (2006) estimated an average mass loss of 27% from a sub 1 km^2 catchment to an 11.4 km^2 catchment, an equivalent export of between 4 and 7.4 Mg C/km^2/yr. Worrall and Burt (2004) found an average net loss of 40% for the River Tees from source to outlet. Worrall et al. (2007), made a complete estimate of fluvial carbon flux for England and Wales. The study estimated that the carbon export, via rivers, from England and Wales is 10.34 Mg C/km^2/yr with 4.19 Mg C/km^2/yr of this going to the atmosphere.

3.3 DOC removal/addition in low order streams

It is considered that the majority of this apparent fluvial carbon loss occurs at a scale of less than 1 km^2 (Moran and Zepp, 1997). Within low-order streams there are a range of processes that could remove, degrade or add DOC to the flux (Fig. 3.1). This study considered those processes that act on a zero and first order drain scale. Firstly, it assessed the influence of these processes at this scale and secondly, assessed to what extent the loss in DOC flux recorded post blocking and the loss in DOC concentration with increasing scale can be explained by these natural processes. In addition to the processes shown in Figure 3.1, at scales larger than those considered in this study DOC may be added to the system from anthropogenic sources and the flux affected by equilibrium with mineral and amorphous phases.

The processes acting in low-order streams are:

i) Biodegradation (Breuer et al., 1997)
ii) Photodegradation (Mostafa et al., 2005)
iii) In-situ production (Obernosterer et al., 2004)
iv) Release from POC (Evans et al., 2005)
v) Flocculation (McKnight et al., 1992)

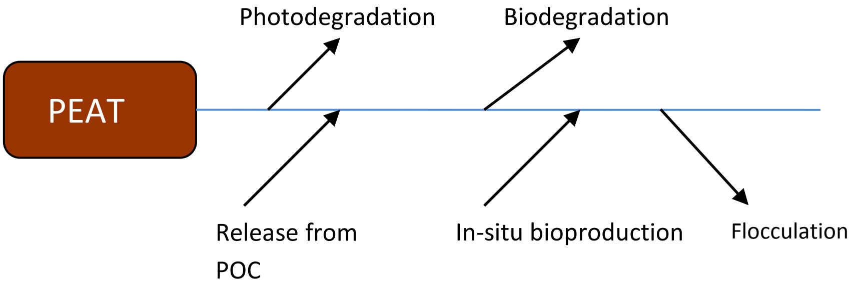


FIG. 3.1: Schematic view of removal and addition processes acting within low-order streams

3.3.1 Biochemical degradation

Biochemical degradation involves the aerobic decomposition of organic matter (including DOC) in the water column or at the sediment-water interface by in-stream micro-organisms (Breuer et al., 1997). This process leads to a reduction in the dissolved oxygen (DO) within the water body. The biochemical oxygen demand (BOD) gives an approximate determination of the amount of DO required by aerobic micro-organisms to break down the organic material contained within a water or wastewater sample (Velz, 1984). Values of BOD range from under 1 mg/l in some unpolluted waters, to around 600 mg/l for raw sewage and 25000 mg/l for paper pulping waste (Reeve, 1994). The BOD measures oxygen concentration decline over a known period of time meaning it is essentially also measuring DOC loss and CO_2 production, therefore, it represents a measure of the rate of DOC loss (Wright, 2003).

3.3.2 Photodegradation

Photodegradation is the degradation of photodegradable molecules to CO_2 and CO as well as other low-weight molecular mass products. This is caused by the absorption of photons, particularly at those wavelengths found in sunlight such as infrared radiation, visible light and ultraviolet light (Mostofa et al., 2007). However, other forms of electromagnetic radiation can cause photodegradation for example x-rays or gamma rays (Mostofa et al., 2005). Photodegradation includes photodissociation, the breakup of molecules into smaller pieces by photons (Tylie and Smith, 2001); the change of a molecule’s shape to make it irreversibly altered, such as the denaturing of proteins; and the addition of other atoms or molecules. Rates of photodegradation in the field are generally reported for long residence time systems e.g. lakes (Kopacek et al., 2003) or estuaries (Moran et al., 2000). Rates of approximately $9 \times 10^{-3} – 0.4$ mg/l/day have been reported in surface waters (Graneli et al., 1996). However, photodegradation can be catalysed by the presence of other chemical species especially Fe (Brinkman et al., 2003) and cannot be considered independent of biodegradation (Evans et al., 2006).

3.3.3 In-situ production

In-stream fauna and flora have the potential for autochthonous DOC production. Obernosterer and Benner (2004) have reported that autochthonous DOC is less prone to biodegradation and less prone to photosensitisation for biodegradation.

3.3.4 Release from POC

The solubility of DOC is enhanced at higher pH (Lumsdon et al., 2001), therefore peat particles being moved in the streams could release DOC absorbed to them as they cross the transition between low and high pH stream waters. Fluxes of POC in peat-covered catchments have been reported as high as 200 Mg C/km^2/yr (Evans and Warburton, 2005).

3.3.5 Flocculation

DOC can be removed from solution by flocculation especially in the presence of Fe and Al (Sharp et al., 2006). Higher order peat stream trend to be an acidic pH that although low in ionic strength does mean that Fe and Al can be mobile with a consequential potential for flocculation later. Fe/Al compounds are mobile at low pH but would precipitate at higher pH, the binding of DOC to these molecules as precipitation occurs would result in a loss of DOC from the stream. McKnight et al. (1992) showed that such mixing of streams resulted in an average 40% removal of DOC.

3.4 Dissolved Carbon Dioxide

The exchange of CO_2 between surface water and the atmosphere can be a significant source or sink of CO_2 to the atmosphere on a global or regional scale (Sarmiento et al., 1992; Cole et al., 1998). Excess CO_2 in upland waters will affect the downstream chemistry by increasing the buffering capacity of the river. This has impacts on water treatment works, where an increase in buffering capacity would require changes in added lime to neutralise this buffering capacity thus making water treatment more expensive (Fleck et al., 2004). This study considers the levels of dissolved CO_2 in stream water produced by the degradation of DOC.

3.4.1 Sources of dissolved CO_2 from upland peat in drainage waters

There are four main sources of CO_2 which contribute to drainage waters. Firstly, CO_2 is produced within the soil pore spaces as part of soil and root respiration. The amount of CO_2 produced has been linked to the aerobic volume of the peat (Skiba et al., 1991) thus the greater the volume of aerobic peat the greater the amount of CO_2 produced (Van Huissteden et al., 2006). The CO_2 produced in the soil will partition between the soil, atmosphere and the water present in the pore, and therefore the greater the amount of CO_2 dissolved into the soil pore water (Dawson et al., 2002). This soil pore water is then either flushed or flows into the drainage system (Clow et al., 1996). Often the dissolved CO_2 concentration in the soil water is in excess of the CO_2 concentration in the atmosphere leading to CO_2 fluxing directly from the surface waters in to the atmosphere (Pinol et al., 1992). Secondly, CO_2 can be added from the atmosphere which will equilibrate with all open waters. The third source of CO_2 into drainage waters is from geological sources (Cole, 1998). If the underlying geology of an area is carbonate based then as the carbonate weathers, calcium carbonate ($CaCO_3$) will dissolve into the drainage waters (Worrall et al., 2005). Finally, dissolved CO_2 is produced internally within the stream by the turn over of DOC.

3.5 Methodology

This study aimed to consider the fate of DOC within low-order peat streams. The significance of those processes outlined above was assessed in order to estimate to what degree the decrease in DOC export post blocking is due to the effects of drain blocking and not to these natural processes. Specifically, the study considered the effects of the biodegradation, photodegradation and the addition of dissolved carbon dioxide. This study did not directly consider the contribution of POC degradation either indirectly via production of DOC or directly to CO_2. This is not to deny the existence of these processes rather that this study is based on the dynamics of DOC and does not base its argument on POC budgets at varying scales. However, processes of POC degradation would be included in the tests of biodegradation as unfiltered samples were used.

3.5.1 Biodegradation

The BOD is determined by measuring the DO of a sample (either iodometrically or potentiometrically) before and after incubation in the dark, in airtight bottles, under defined conditions for a specified duration and normally with a nitrification inhibitor. Several standard methods exist with a range of variations in those conditions and incubation periods (Young et al., 1981; National Council of the Paper Industry, 1982; ISO, 1990), but the most commonly used methods run over 5 days (BOD_5) and are based on the original United Kingdom Royal Commission on Sewage Disposal method. The method can be subject to errors from the additional use of oxygen by nitrifying bacteria to oxidise ammonia to nitrite and nitrate, thus a nitrification inhibitor (e.g. allythiourea - ATU)) may be added to samples containing ammonia (e.g. river waters).

FIG. 3.2: Use of dissolved oxygen meter during a BOD experiment

The standard method from "Methods for the Examination of Waters and Associated Materials: 5 Day Biochemical Oxygen Demand ($BOD_{5\text{-}DAY}$)" (HMSO, 1998) was used for all BOD analysis in this study. BOD incubations were initiated a maximum of 6 hours after sample collection during all water quality surveys, and analyses were carried out on well mixed unfiltered samples. Dissolved oxygen readings were taken potentiometrically using a dissolved oxygen meter and ATU was used as a nitrification inhibitor. Bottles were securely stoppered and incubated in a temperature controlled room (20°C +/- 10%) in the dark. This method had an error of approximately ±1.5%. No sample pre-treatment for the presence of algae, chlorine, ferrous iron, hydrogen sulphide or sulphur dioxide, or high total suspended solids were deemed necessary for any of the samples. On each field visit a stream water sample was collected from each of the monitored drains on Cronkley Fell. These were then transported back to the lab for analysis.

3.5.2 Alternative degradation experiments

The surface waters in this study are open to influence from photons of light and their subsequent degradation effects. This means in order to create an accurate insight in to the effects natural degradation has on the overall DOC export any proportion of change post blocking caused by photodegradation must be accounted for. Several methods have been used to determine the level of photodegradation in water samples. Waiser and Robarts (2004) incubated water samples in polystyrene culture bottles on racks in large flow through water baths. Samples were open to the effects of natural sun light and the DOC concentration was measured both pre and post incubation to determine the effects of solar radiation on dissolved organic matter in the samples.

Selections of samples were wrapped in aluminium foil so experiments could be performed in the dark as a control. Similarly, Lange et al. (2003) and Larson et al. (2007) measured the change in DOC concentration after incubation in glass bottles. This study follows the method of Mostofa et al. (2007) where level of photodegradation will be determined by the change in DOC concentration over a set period of time with samples incubated in quartz (uv transparent) photo tubes. The quartz tube allow light to pass through to the sample but prevent dilution from occurring. It is important to note that although these experiments were performed to estimate levels of photodegradation the change in DOC concentration during the incubation in the quartz tube reflects both biochemical degradation and photodegradation.

Quartz tubes were taken into the field where they were filled with stream water samples and secured at each end with a rubber bung. A small amount of air was left at the top of the tube to allow oxidation to occur. These sample tubes were then left in the field for varying periods of time between 7 and 63 days. Samples were taken in duplicate from one zero order (CR1 and CR6) and one first order drain (CR4 and CR3) in the experimental and control catchment on Cronkley Fell.

FIG. 3.3: A quartz tube experiment at the experimental catchment on Cronkley Fell.

No attempt was made within this experiment to create a sterile control, however, control samples were taken and the quartz tubes wrapped in aluminium foil in order to exclude light. The amount of photodegradation would then be calculated as the difference between light and dark samples. Samples were located in hollows to prevent undue disturbance by the weather and fauna and weighed down with rocks.

The DOC concentration was taken at the start of the experiment by the Bartlett and Ross (1988) method discussed in chapter 2. This was then compared with the DOC concentration at the end of the experiment. Conductivity and pH were also measured using handheld electrode methods. Solar radiation as PAR along with temperature was also monitored semi continuously during this period. A temperature probe (Campbell Scientific 107 temperature sensor) and PAR gauge (Campbell Scientific SKP 215 Quantum Sensor) were wired into a data logger. The data logger was programmed to record each variable every 15 minutes; this data was then downloaded to portable p.c. on each field visit. This method had an approximate error of ±1.5%.

3.5.3 Dissolved carbon dioxide

The amount of dissolved CO_2 leaving the peat is calculated by modelling the speciation of inorganic carbon within the drain samples. Once the different species within the complex river system have been constrained the excess concentration of dissolved CO_2, where excess is defined relative to the atmosphere, in the river waters can be calculated (Rowson, 2007). To measure these different components of the speciation model, several basic measurements need to be taken, these are; pH, alkalinity or acidity (depending upon pH of the streamwater), total calcium concentration (mg Ca/l), total aluminium concentration (mg Al/l), DOC concentration (mg C/l) and water temperature (K). This information can be used to construct a speciation model, to predict the concentration of the different ions in the sample from which the excess partial pressure of CO_2 in the sample can be found. Depending upon the pH of the samples either acidity or alkalinity is measured. If the pH of a sample is below 5.5 then acidity is measured, if the pH is above 5.5 then the alkalinity is measured (Stumm and Morgan, 1981; Butler, 1982).

Samples of surface water from blocked and unblocked drains at all scales were collected in the field and analysed on the same day in the laboratory for pH and alkalinity or acidity depending on the sample pH. The pH was determined using a handheld electrode method with an error of ±0.01 pH. A small sample was retained for analysis by ICP OES (Inductively Coupled Plasma Optical Emission Spectrometer) for calcium and aluminium concentrations. Analysis was performed on filtered samples using a Perkin and Elmer Optima 3300 RL ICP-OES machine and ICP Winlab was used for machine control and data processing. Mixed standards for analysis were produced using Romil ICP standards and a serial dilution technique.

Standards (including blanks) were run prior to analysis and the 50 and 25 mg/l standards were re-analysed as samples every 25 samples as a manual check for drift.

The range of the pH of the water samples meant that acidity was measured for all samples rather than alkalinity. For samples with the highest pH alkalinity measurements were also taken but no significant difference with the acidity measurements was found thus acidity was used for all samples. Acidity was measured using a titrometric method in which 30 ml of a sample was taken to which a 0.1 M solution of sodium hydroxide (NaOH) was added drop wise. Phenolpthalien was used as an indicator to determine the end point of the reaction. This determined the overall buffering capacity of the solution. This method had an associated error of approximately ±5%.

3.6 Statistical Analysis

The data collected was tested by analysis of variance (ANOVA). The ANOVA was used in a series of separate analyses. First, BOD was considered along with the following factors: scale, month of the year and blocking status. The month factor has 12 levels, one for each month of the year. The scale factor has two levels, zero and first order, and the drain-blocking factor has two levels, blocked and unblocked. The second analysis was performed on the results from the quartz tube experiments. The change in the DOC concentration during the incubation period was considered with scale, month of the year, blocking status, length of incubation and whether the experiments were performed in the light and dark. DOC concentration at the start of the experiment, pH and conductivity were considered as covariates. The third analysis was performed on the dissolved CO_2 data. The analysis considered the factors of month, scale and blocking. The error terms associated with these ANOVA's were calculated however it is important to stress that the error term in ANOVA represents the unexplained variance and is not just a matter of sampling or measurement error; it could for example represent factor interactions that could not be estimated in this study.

The data was also subjected to a process of multiple regression. Regression was used to establish whether there was a significant correlation between the loss in DOC concentration as the water moved through the system and the extent of DOC degradation i.e. the level of photodegradation and the BOD, and the experiment length. The data was first put through a process of stepwise regression. This can establish which correlations are significant. Stepwise regression is limited as parameters included in the regression which have no significant correlation can prevent the identification of those parameters with better correlations. Also multi-collinearity can arise when predictor variable are inter-correlated. This makes the signs and magnitudes of the regression coefficients unstable.

To reduce these problems significant correlations were then put through a process of normal regression to discover how significant the relationship is and what the equation for this would be: for this the R^2 value was used. The R^2 indicates how well real data points fit a regression line. Thus it is a measure of the variance explained. Therefore R^2 represents the proportion of the variance explained by the particular linear regression.

The level of dissolved CO_2 was calculated using the method of Neal and Hill (1994). The DIC speciation was determined from the Gran-acidity ($G_{acidity}$). For this study $G_{acidity}$ is defined by following charge balance equation:

$$G_{acidity} = 2H_2CO_3^0 + HCO_3^- + 4Al^{3+} + 3Al(OH)^{2+} 2Al(OH)_2^+ + Al(OH)_3^0 + 2AIF^{2+} + AIF_2^+ + 4Alorg^+ + 3Al(OH)org^0 + H^+ + NH_4^+ + Horg^- + 2H_2org^0 - OH^- \tag{1}$$

3.7 Results

3.7.1 Biochemical degradation

The $BOD_{5\text{-}ATU}$ was calculated for all localities on Cronkley Fell for a series of 20 field visits from July 2008 until April 2010. A total of 120 samples were analysed. The $BOD_{5\text{-}ATU}$ results were seen to vary from a maximum of 13.0 mg O_2/l on the experimental zero order drain to a minimum of 0.3 mg O_2/l on the experimental first order and a maximum of 7.2 mg O_2/l on the control zero drain to a minimum of 0.5 mg O_2/l on the control first order stream (Fig. 3.4). A similar decline in $BOD_{5\text{-}ATU}$ from zero to first order drains can be seen in the median values for both catchments with the control catchment demonstrating a decline of 5.4 mg O_2/l on the zero order drain to 1.6 mg O_2/l on the first order drain. However, this reduction of $BOD_{5\text{-}ATU}$ with scale is smaller on the experimental catchment with a median $BOD_{5\text{-}ATU}$ of 4.9 mg O_2/l being recorded at the zero order drain and 3.36 mg O_2/l being recorded at the first order drain.

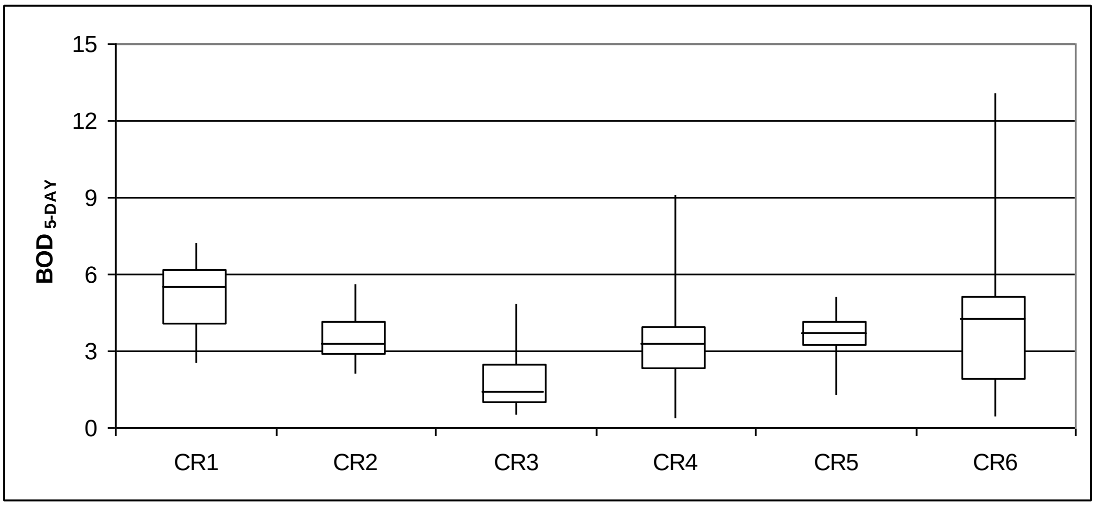


FIG. 3.4: Box and whisker plots of $BOD_{5\text{-}ATU}$ (mg O_2/l) for the control and experimental catchment on Cronkley Fell.

The analysis of the mean $BOD_{5\text{-}ATU}$ values for the control catchment and experimental catchment in the pre and post blocking period (Fig. 3.5) again indicates a decrease in the recorded $BOD_{5\text{-}ATU}$ upscale demonstrating that DOC is indeed being lost from the system via biochemical degradation as the water moves down the catchment. The decrease in the $BOD_{5\text{-}ATU}$ from CR1 to CR3 can explain an approximate decrease in DOC concentration of 3 mg C/l during a 5 day incubation when water travels from zero to first order drains. However, it is important to note that it does not take water 5 days to flow from zero to first order which means the actual average daily loss in DOC due to biochemical degradation is significantly smaller. An average decrease of 0.34 mg C/l/day due to biochemical degradation was calculated from all collected $BOD_{5\text{-}ATU}$ data. The average loss of DOC from the zero to the first order drain on the control and experimental catchment is 25 mg C/l and 20mg C/l respectively. As such the effect of biochemical degradation on the overall carbon budget for the area would be small.

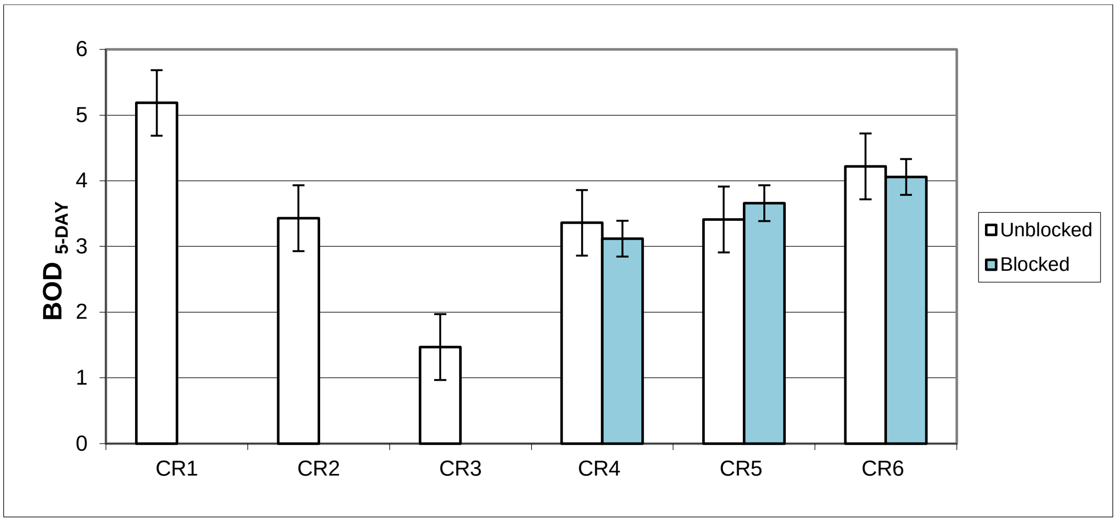


FIG. 3.5: The mean $BOD_{5\text{-}DAY}$ (mg O_2/l) for the monitored drains on Cronkley Fell.

The data collected was subjected to a process of ANOVA (Table 3.1). The analysis found scale and month to be significant. The month factor explains the majority of the variance but the error term still explains 35.1% of the variance in BOD value. The significance of the monthly factor indicates the change in microbial activity or DOC composition during the year with warmer months likely to have higher levels of activity thus higher BOD values then cooler months. The scale factor shows co-linearity with site and the scale factor's significance in the ANOVA analysis reflects the reduction in BOD observed at increasing scale shown in Figures 3.4 and 3.5. Scale was used as a factor in the ANOVA rather than site because unlike the ANOVA performed on the DOC budget data in chapter 2 this experiment does not use data from the pristine catchment at Atkinson Moss where monitoring occurs on a natural stream which cannot be accurately categorized as either a zero or first order drain. In this degradation experiment all data collected was from Cronkley Fell where drains can be easily identified as either zero or first order. Blocking of the drain was not found to be a significant factor in level of biochemical degradation.

Factor	P	Proportion of variance (%)
Month	<0.001	35.7
Scale	<0.001	31.2
Blocking	>0.5	
Error		33.1

Table 3.1: ANOVA of $BOD_{5\text{-}DAY}$ *for all monitored sites and months giving the probability of the factor and the proportion of the variance explained by the factor.*

3.7.2 Alternative degradation experiments

The effects of sunlight on DOC degradation was measured for both one zero and one first order drain in the control and experimental catchments on Cronkley Fell. A series of 15 experiments were run from March 2009 until April 2010 with 240 samples being analysed. The length of time the samples were incubated for in the field was not constant due to limitations related to site access such as weather conditions or shooting schedules. Despite these limitations a correlation between experiment length and total change in DOC is recorded (Fig. 3.6) indicating that the method is sound.

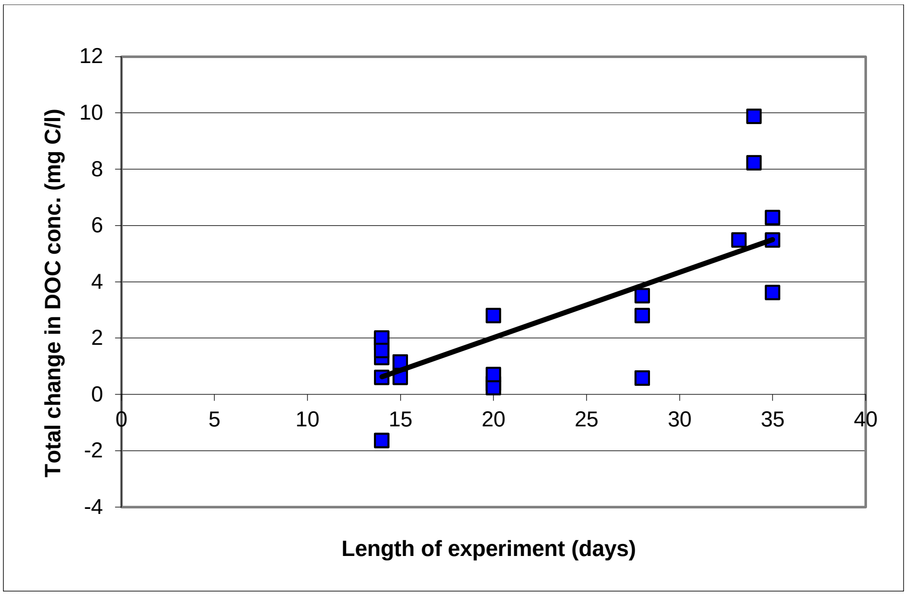


FIG. 3.6: The correlation between the length of experiment and the total change in DOC concentration during the experiment incubation period. Best fit line: y=0.2315x – 2.6082, R^2*=0.5463.*

To enable comparisons of the results of the quartz tube experiments from different sites, scales and light or dark conditions the total change in DOC was converted into the change in DOC per day by division by the length of the experiment. The range of the results for most of the experiments performed in the light (Fig. 3.7) and dark (Fig. 3.8) showed a small loss in DOC during the incubation with the median values for the experiments in light varying from a daily loss in DOC of 0.14 mg C/l/day to 0.19 mg C/l/day and experiments in the dark varying from a daily loss in DOC of 0.06 mg C/l/day to 0.11 mg C/l/day. However, examination of the experiment detail shows that the influence of photodegradation is complex with several of the box plots in Figures 3.7 and 3.8 indicating negative minimum values i.e. the DOC concentration has increased during the incubation period. This is indicative of a DOC production or desorption from POC and the presence of DOC producing organisms in the water.

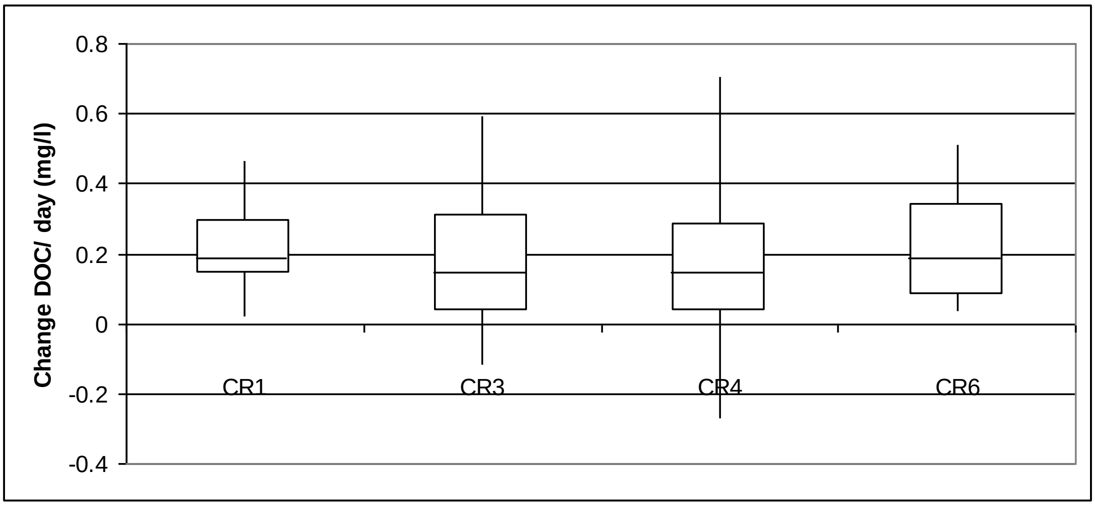


FIG. 3.7: Quartz tube experiments for the control and experimental catchments on Cronkley Fell. The results reflect experiments performed in the light.

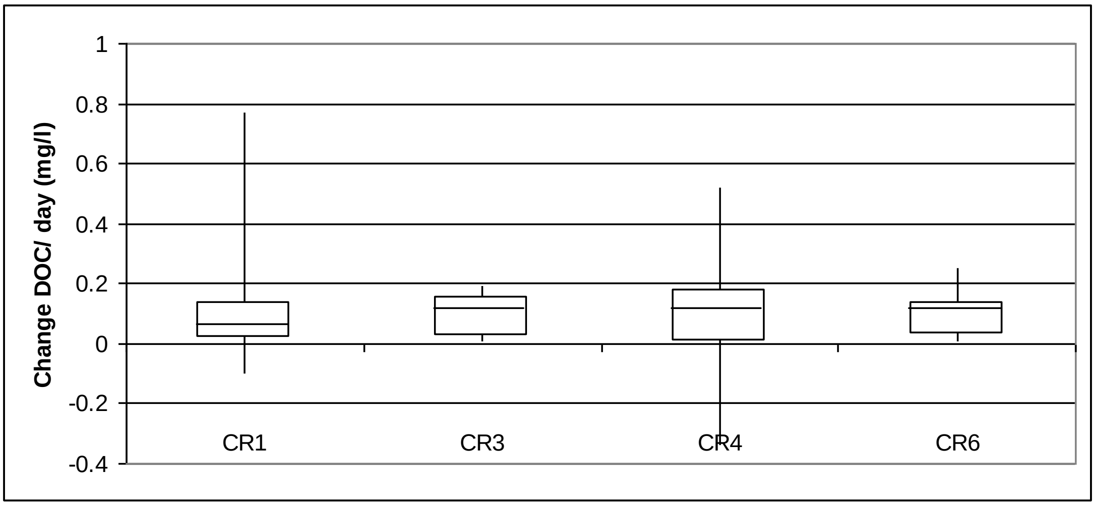


FIG. 3.8: Quartz tube experiments for the control and experimental catchments on Cronkley Fell. The results reflect experiments performed in the dark.

The data collected was subjected to ANOVA (Table 3.2). The analysis found that when the DOC concentration at the start of the experiment, pH and conductivity are considered as covariates the change in DOC during the quartz tube experiments was significantly affected by the conditions of the experiment (was the experiment performed in the light or dark), the month, the length of the experiment, the DOC at the start of the experiment, pH and conductivity at the 95% probability. The conditions of the experiment explain the majority of the variance which is to be expected as when experiments are performed in the dark the likelihood of photodegradation is very low or zero. The error term explains 16.8% of the variance in the daily change in DOC concentration. The significance of the month factor reflects natural seasonal changes in light levels during the year. As indicated by the ANOVA conductivity and pH are significant covariates. During the quartz tube experiments the conductivity is seen to decrease and the pH increase. This is unusual as an increase in conductivity would be expected. One possible cause of this may be the degassing of the water sample. Also it may be explained by the consumption of any carboxylic acid by microbes which would lead to a decrease in conductivity and an increase in pH.

Factor	P	Proportion of variance (%) with DOC at start of experiment, pH & Conductivity	Proportion of variance (%) without DOC at start of experiment, pH & Conductivity
Light/Dark	<0.001	28.1	33.2
Month	<0.001	18.7	21.6
DOC at start	<0.001	14.2	
Length of experiment	<0.001	11.9	15.9
pH	<0.001	7.1	
Conductivity	<0.001	3.2	
Blocking	>0.5		
Scale	>0.5		
Error		16.8	29.3

Table 3.2: ANOVA of DOC concentration change during quartz tube experiments for all monitored sites and months giving the probability of the factor and the proportion of the variance explained by the factor.

When the DOC at the start of the experiment, pH and conductivity are excluded from the analysis the conditions of the experiment, month and length of the experiment are found to be significant with the majority of the variance being explained by whether the experiment is performed in the light or dark and an increased importance of the error term of 29.3%. Blocking of the drain or scale was not found to be significant. This is to be expected as the process of drain blocking will not affect the amount of sunlight which will reach the ground also the catchments studied are both less than 1km^2 meaning that light levels are unlikely to vary drastically over such a small area. Multiple regression was used to produce an equation to predict the amount of DOC lost to the atmosphere.

$$\Delta DOC = 4.9DOC_0 + 0.17t - 19.2 \quad (1)$$

Where: ΔDOC =Total change in DOC concentration; DOC_0 =DOC concentration at the start of the experiment; and t = Time

When the mean values of time and the DOC concentration are inputed in to the above equation an average loss in DOC due to degradation in the quartz tubes of 0.73 mg C/l/day is calculated. The combined effects of both biochemical and photodegradation although small are still statistically significant. However, it is clear that the reduction in DOC concentration upscale and the reduction in DOC export post blocking recorded for Cronkley Fell can not solely be explained by degradation alone and the effects of dilution and water mixing must also be acting on the system.

3.7.3 Dissolved CO_2

A total of 48 water samples were analysed for levels of dissolved CO_2. The experiments were performed on one zero and one first order drain in both the experimental and control catchment. Experiments in the experimental catchment were only performed post blocking. Comparison of the results from the control and experimental catchment show that the level of dissolved CO_2 did not vary greatly between scale and blocked and unblocked catchment (Fig 3.9). A mean value of 0.3 mg C/l is recorded across the sites. It is also interesting to note that some of the values recorded are negative. Negative values of dissolved CO_2 indicate that the catchment is taking in CO_2 possibly caused by the interaction of the water with non-carbonate rocks or mineral horizons in the soil.

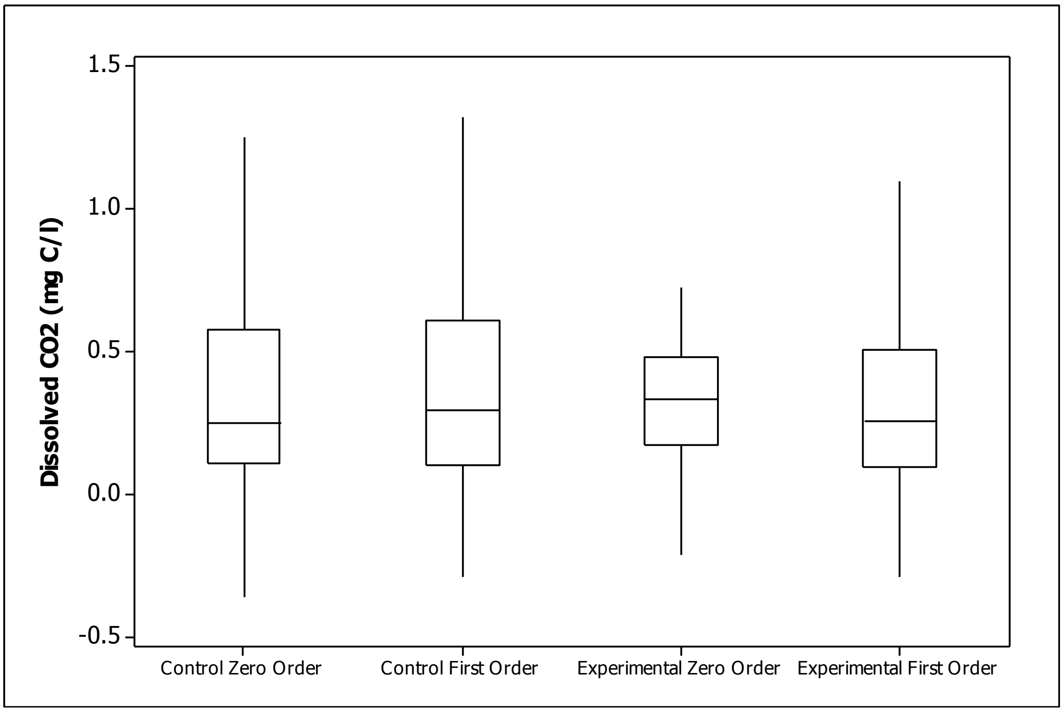


Fig. 3.9: Comparison of levels of dissolved carbon dioxide across the experimental and control catchment at Cronkley Fell.

Factor	P	Proportion of variance with pH and conductivity (%)
Month	<0.001	34.4
Scale	>0.5	
Blocking	>0.5	
Error		65.6

Table 3.3: ANOVA of dissolved CO_2 giving the probability of the factor and the proportion of the variance explained by the factor.

ANOVA of the dissolved CO_2 found that the results were significantly affected by month (Table 3.3). This significant month effect reflects a seasonal cycle in the dissolved CO_2 content of the drain water. Scale and blocking were not found to be significant. The error was found to explain 65.6% of the data.

3.8 Discussion

This chapter aimed to assess the influence of those factors such as DOC degradation and carbon dioxide dissolution, which will increasingly affect the DOC budget as scale increases. The effects of photodegradation and biochemical degradation on DOC loss are small with the quartz tube experiments indicating a combined loss of 0.73 mg C/l/day. The level of dissolved CO_2 is equally small with a mean value of 0.3 mg C/l. It is clear that the reduction in DOC concentration upscale, discussed in the previous chapter, can not solely be explained by degradation alone and the effects of dilution and water mixing must also be acting on the system. If these processes were to be occurring this would have important implications for the efficiency of any drain blocking.

The data has shown that degradation of DOC in the catchment is very close to zero yet results from the BOD experiments indicated that that the level of degradation changes with scale. Since the level of degradation is very close to zero to see any actual change in the level of degradation with scale would be unlikely. As such it is considered that a compositional change in DOC must be occurring in the catchment to account for the significance of scale in the BOD ANOVA. This compositional change may be the result of additional water being added to the system or changes in flow pathways post blocking. This potential source of water is considered in chapters 4 and 5.

The size of the influence of DOC degradation in the study catchments may reflect their relatively small spatial area. The control and experimental catchments are 0.750 km^2 and 0.715 km^2 in size respectively and hydrological studies (Chapter 4) of the area have shown that water in the drains has a tendency to move relatively swiftly through the system and out of the catchment meaning there is a limited period of time for the DOC in the water to be subjected to the processes of degradation. Therefore, the influence of degradation may be more obvious when studied at larger catchment scales. However, for a river such as the Tees where the complete travel time from source to mouth is only a few days DOC degradation will still only have a small effect on overall DOC loss meaning that the loss in DOC mass during this period still remains unexplained.

3.9 Conclusion

1. Biochemical degradation is found to have only a small influence, approximately 0.34 mg C/l/day, on DOC moving from zero to first order drains.
2. The quartz tube experiments indicated that the effect of photodegradation was equally small with a combined biochemical and photodegradation loss of approximately 0.73 mg C/l/day.
3. It is clear that the combined effects of DOC degradation can not solely explain the decrease in DOC concentration seen from zero to first order drains in the study catchments and the effects of dilution and water mixing must also be acting on the system
4. There was no observed effect of drain-blocking on the level of degradation.

4. The physical hydrology of a blocked upland sub-catchment

4.1 Introduction

The hydrology of upland catchments is controlled by a complex system of water sources and flow pathways. The water leaving the demonstration catchments at Cronkley Fell will reach this point by flowing through the drains as well as via surface runoff and as flow through the soil itself. Small contributions of water may also be added to the system from deeper water that could be referred to as groundwater. The purpose of drain blocking is to slow the movement of water through the system and raise the water table thus regenerating the peat and reducing DOC export. This chapter will firstly examine whether drain blocking has the desired effect on water table and whether a change of similar magnitude in the water table was visible at a larger first order drain scale.

Having examined changes in the water table, this chapter will consider the effect of blocking on the fluvial hydrograph of the catchment. The hydrograph of a catchment is controlled by the duration and intensity of a rainfall event and the flow pathway taken by the water through the system. The blocking of drains may lead to a change in the water balance and a shift in flow pathways. At some point it is likely that the drain will cut across the slope. As the drain is crossing the slope the water in the channel will tend to flow down slope under the force of gravity taking any DOC with it and so bypassing the blockages and entering the surface waters of the catchment elsewhere. The bypassing of flow around the blockages means that any effect of drain blocking seen on an individual drain scale may be lost when the effects are examined at catchment scales.

4.2 The hydrology of upland catchments

4.2.1 Hydrological effect of drainage

As stated in chapter 1 the key aim of peatland drainage in the UK was to lower the water table in the peat resulting in a firmer surface more suitable for certain vegetation types that are themselves the preference diet of grazers while at the same time making the soils less vulnerable to the action of trampling by grazers. However, due to the low hydraulic conductivity of peat and the often low relief of the areas over which they are found the water table is generally not found to drop in the manner which was originally desired (Stewart and Lance, 1991).

Studies dating back as far as the eighteenth century have suggested that peatlands store water in a similar manner to a sponge, soaking up water during storms and releasing it gradually over a significant period of time, thereby reducing flow peaks and sustaining baseflows (Turner, 1757). However, the opposing view has been demonstrated by many more recent studies, showing that the water table rarely drops far enough in blanket peats that substantial storage capacity would be available to attenuate flood peaks (Eggelsmann, 1971). This supports observational data that blanket peats produce a great deal of run off with extremely flashy hydrographs and relatively small baseflow contributions (Evans et al., 1999).

A flashy hydrograph may seem to suggest that waterlogged peats can easily be made to give up their water and that drainage should be successful, probably adding further to the flashy nature of the hydrograph response. However, many studies have shown that the vast majority of flow in peats takes place over the surface and through the upper few cm (Holden and Burt, 2003b). Drainage may well play a part in increasing the flashy nature of the hydrograph response by increasing surface runoff as overland flow has only to travel as far as the nearest drain channel before it is rapidly removed, with flow in drains being even faster than flow over the peat surface or through the near surface layers (Holden et al., 2008). However, the implication of this near-surface dominated flow is also that the water table drawdown caused by a drain may not extend a great distance laterally from the drain. Any drop in the water table caused by lateral flow from the peat layers into the side walls of a drain channel will be slow enough that it is easily replenished by infiltration from above. Sillins and Rothwell (1998) also made the point that drainage is likely to lead to some subsidence and compaction of the peat layers, which will decrease hydraulic conductivity and increase water retention, acting against the aim of drainage by limiting flow of water into the drain channels.

4.2.2 The hydrological effect of drain blocking

Several studies have considered the effect of drain blocking on the surrounding water table and drain water yield. Gibson et al. (2009) found that the blocking of peat drains caused a significant decrease in the depth to the water table, i.e. water table moved nearer the peat surface, and a 39% decrease in the water yield flowing through the drain. This decrease in water yield is used to explain the 20% decrease in DOC export also recorded by the study. Wallage et al. (2006) found drain blocking decreased water yield by 35% and Glatzel et al. (2003) recorded a 45% decrease in water yield post blocking. However these studies do not consider the issue of scale and with it the issue of water balance.

Wilson et al. (2010) considered the effect of drain blocking on a Welsh upland blanket bog at landscape scales. The study found that the water table and water storage increased post blocking but these responses showed robust catchment scale difference Wilson et al. (2010) states that "*the increases in water storage after restoration produced lower discharge rates observable at the level of both drain and hill stream; as well as greater water table stability, reduction in peak flows and increases in water residency after rainfall*".

Wilson et al. (2011) considered the impact of drain blocking on an upland blanket bog during storm and drought events for the same catchments in mid Wales. The study found that water tables increased and became less variable post drain blocking intervention indicating that the bog was less susceptible to run dry during drought periods. Wilson et al. (2011) suggests that "*restoration leads to a more buffered system, with more moderate responses to extreme events, and reduced release of both dissolved and particulate organic carbon,*"

Even with the increased water tables across the whole of the drain catchments an increase in evapotranspiration would be unlikely to account for all of the reduction in water yield indicated by Gibson et al. (2009), Wallage et al. (2006) and Glatzel et al. (2003) and thus close the water budget. Therefore water not leaving via the drain must be flowing somewhere else. Water leaving a peat soil will be transporting DOC so any such "leakage" would limit the effect of drain blocking upon DOC export.

4.2.3 Alternative flow pathways

Although the excavation of drainage channels was not found to decrease the water table in the manner which was originally desired (Stewart and Lance, 1991), peatlands are sensitive systems and even moderate changes to water tables might influence their chemistry and the cycling of carbon. The dehydration of peat bogs after drainage has been linked to changes in the soil structure and an increase in flow in soil pipes (Holden et al., 2005a). Alternative flow pathways such as soil pipes are created as the soil cracks and degrades while drying due to the increased drainage (Holden and Burt, 2002 a, b). Holden et al. (2007) states *"that this change in soil structure is important for the hydrology, water quality and ecology in moorlands when attempts are made to rewet the soil after drain blocking*". Soil pipes are natural tubes found below the surface of the peat through which water may flow (Worrall et al., 2007). They form important conduits for sediment and other solutes, and are therefore important for river quality and carbon release (Jones, 2004). Several studies have indicated that flow through soil pipes forms a notable large part of the water balance. A study by Jones and Crane (1984) of a peat moor in Wales reported the movement of water through soil pipes accounted for 50% of total streamflow. Holden and Burt (2002c) determined that for a blanket bog in the north Pennines flow in soil pipes accounted around 10% of total streamflow. The extent of soil piping and the size of the individual soil pipes in blanket peats have been shown to increase over time (Holden et al., 2006).

The large extent of soil piping in drained peats must be considered when drain blocking management strategies are employed. Holden et al. (2007) states that "*it may be that damming the drains simply allows more water to enter the pipe networks that have openings on drain floors and sides*". This would lead to the bypassing of water around the blockages reducing the efficiency of the blocking present as the water takes an alternative pathway through the system.

The characteristics of rainfall events can also lead to an increase bypass flow as water moves through the catchment. Bouma et al. (1990) demonstrated by using undisturbed cores in the field that more bypass flow occurs with increasing rainfall intensity, increasing rainfall quantity and at higher surface water contents. Similarly Heppell et al. (2002) found for structured clay soils an increase in macropore flow can be demonstrated with increasing rainfall intensity, rainfall quantity, surface water content, surface relief and surface texture. Holl et al. (2003) demonstrated an increase of 17% in surface runoff events post blocking for a peat bog in South West Germany with the soil becoming quickly saturated during heavy rainfall events, reducing infiltration and leading to water flowing across the surface of the peat.

4.3 Methodology

This study considers three components of the water balance; the water table, surface runoff and drain discharge in order to determine the effects of drain blocking on the hydrology of the catchment. The water table and runoff are monitored by dipwells and runoff traps in the field. The effect of blocking on drain discharge is examined by an event analysis approach (Heppell et al., 2002). The study documents the change in flow conditions during individual storm events observed in the two peat-covered catchments on Cronkley Fell in both the pre and post blocking period. By analysing a large number of events across the seasonal cycle and a range of hydrological conditions a multivariate database of event characteristics was constructed. This database was then analysed to assess the significant controls upon water runoff and whether these controls vary post blocking.

4.3.1 Monitoring programme

A detailed sampling and monitoring program has taken place on both the control and experimental catchment on Cronkley Fell. The control catchment was monitored from September 2007 to April 2010 and the experimental catchment was monitored from December 2007 to April 2010 with the drains being blocked in March 2009. Flow in each drain was monitored as outlined in section 2.5.1. The amount, intensity and duration of rainfall events were monitored by tipping bucket rain gauge which was installed on the control catchment. The water table depth was monitored by a series of dipwells that transect both catchments (Fig. 2.1 –section 2.3.1). The dipwells have an error of approximately ± 2%. On the control catchment on Cronkley Fell 24 dipwells have been installed with an additional 18 dipwells installed on the experimental catchment on Cronkley Fell. These were located such that they formed a profile across the sites cutting across all the monitored drains. The location of individual dipwells is shown in Figure 4.1 and Figure 4.2. A total of 6 dipwells were installed at Atkinson Moss in a transect perpendicular to the natural stream running to the water shed (Fig. 4.3). Dipwells were not installed on Wemmergill. During the monitoring period the depth to the water table was recorded every two weeks.

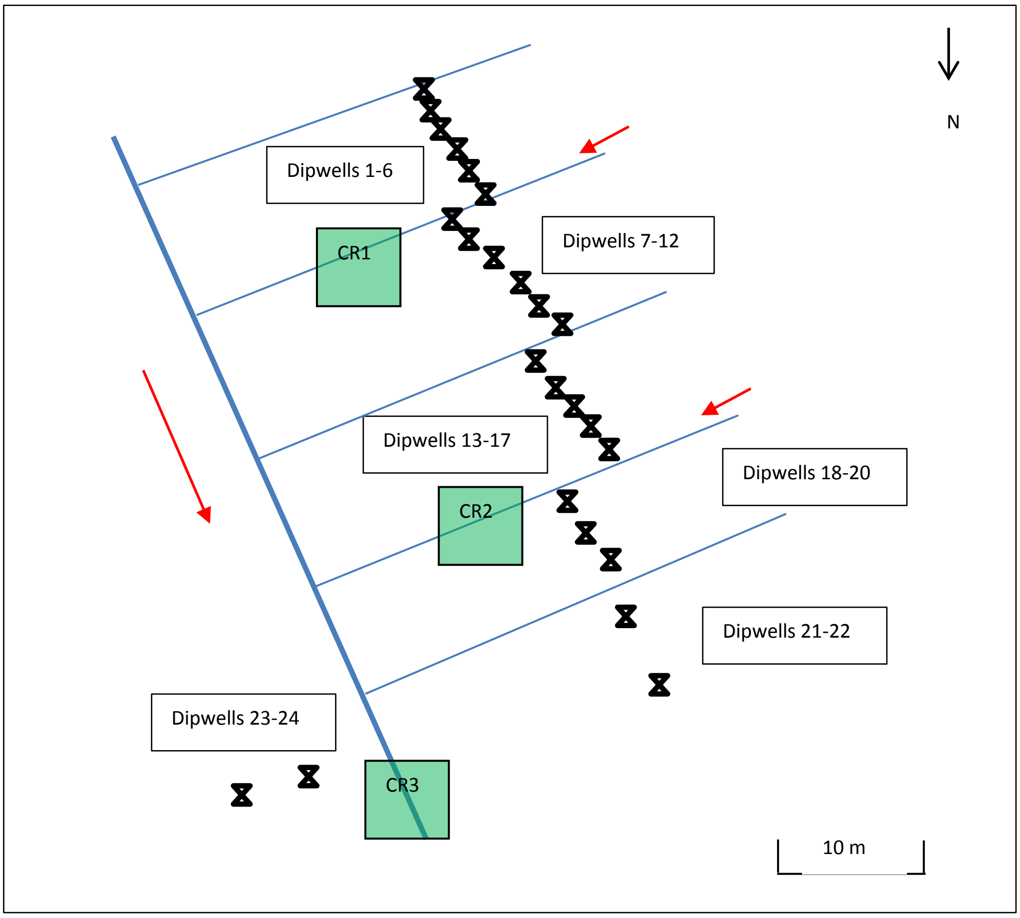


Fig 4.1: Schematic diagram of dipwell location on the control catchment at Cronkley Fell.

First Order Drain ━; *Zero Order Drain* — ; *Flow direction* →; *Monitoring Point* 🟩; *Dipwell* ⧗

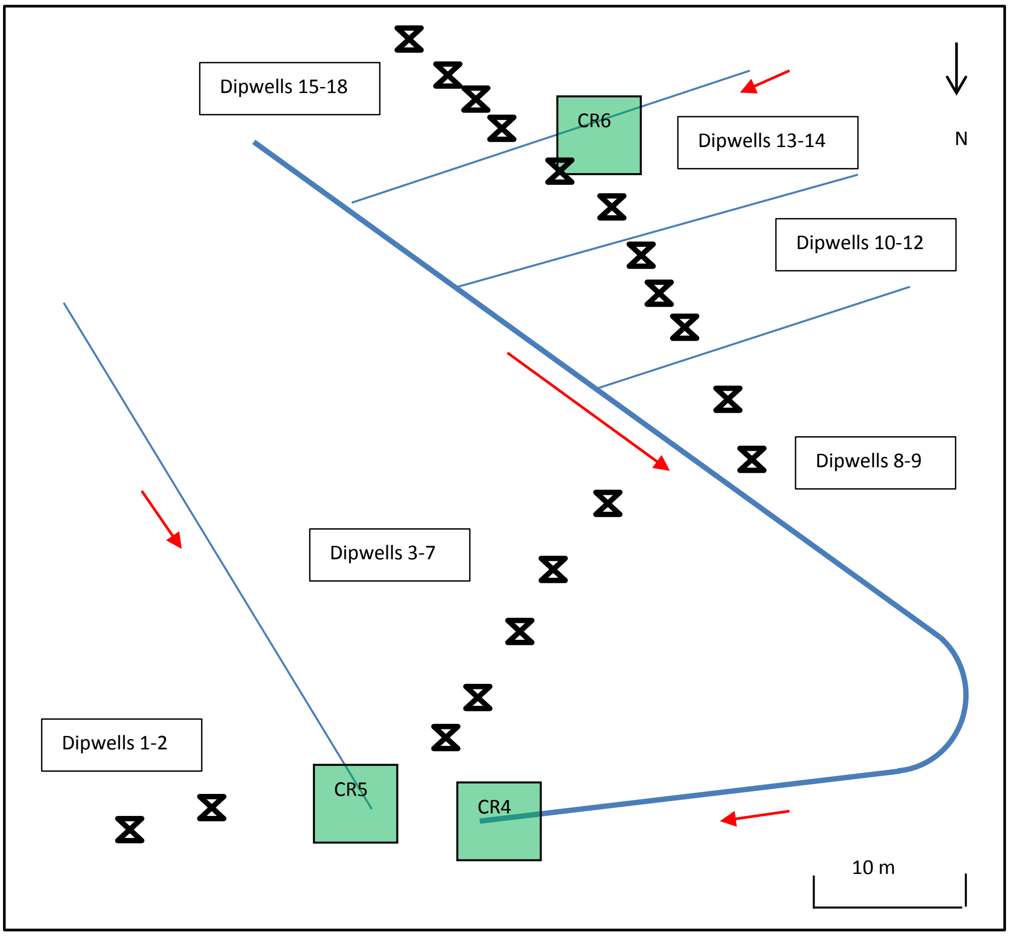


Fig 4.2: Schematic diagram of dipwell location on the experimental catchment at Cronkley Fell.

First Order Drain ▬; *Zero Order Drain* —; *Flow direction* →; *Monitoring Point* 🟩; *Dipwell* ⧗

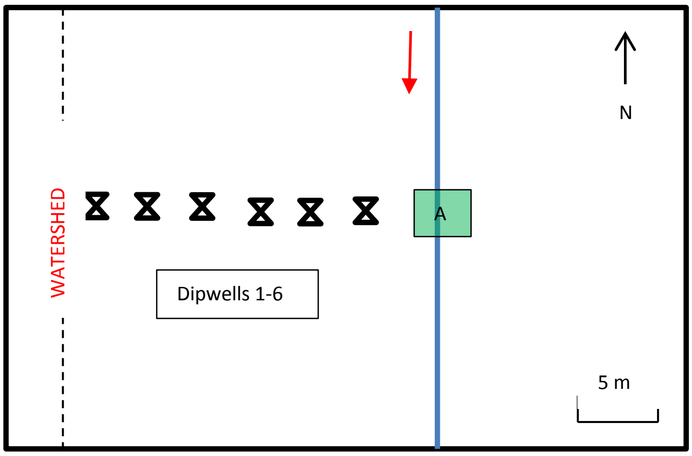


Fig 4.3: Schematic diagram of dipwell location at Atkinson Moss.

Natural Channel ▬; *Flow direction* →; *Monitoring Point* 🟩; *Dipwell* ⧗

The presence of surface runoff was also monitored by the installation of a network of crest fall runoff traps. These were placed in a grid pattern both above and below a monitored drain in the control and experimental catchment on Cronkley Fell. A total 15 runoff traps were installed on the experimental catchment and 32 on the control (Fig 4.4).

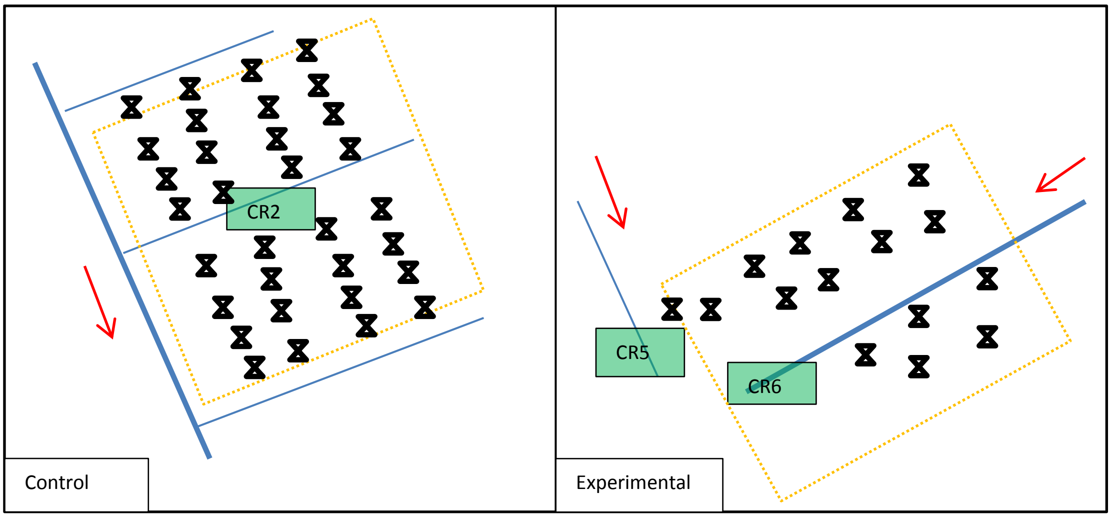


Fig 4.4: Schematic diagram of runoff trap location at Cronkley Fell.
Drain ▬ *; Flow direction* →*; Monitoring Point* 🟩 *Runoff trap* ⧗

The data collected from the monitoring of the water table depth, runoff and drain discharge was subjected to a process of statistical analysis. All measurements were used to calculate the relative water table and relative monthly water yield and export between the control catchment and the experimental catchment in the pre and post blocking period using the same method described in section 2.8. Also the data was subjected to a process of ANOVA (a detailed description can be found in section 2.8) with the factors of month and blocking, and in the case of water yield/export, scale being considered. The runoff data was subjected to proportional analysis with aim of assessing whether the number of overland flow events had increased post blocking.

4.3.2 Event Analysis

The study aims to examine the behaviour of the runoff from the peat and whether the blocking of the drains has a significant effect on this behaviour. If the study examined only change in the nature of surface flow from a peat catchment after blocking then the results could simply reflect changes in precipitation inputs.

Therefore the study needs to examine the change in the relationship between inputs and outputs. This study collates the characteristics of rainfall events and assess for each event whether a flow event occurred and uses statistical modelling to understand the distinction between these two. The study considered rainfall events for the 12 months before and 12 months after drain blocking.

4.3.3 Model Development

The study considered all separate rainfall events which could be identified from the rainfall record. A rainstorm was considered as "*separate*" if there was at least one sampling period of no recorded rain on either side. Given a separate rainfall event, the drain discharge record is examined for the subsequent 12 hours in order to assess whether a flow event has occurred. An "event" was considered to have happened if the drain discharge was observed to increase. Where no such increase was observed the storm was classified as a non-event although for all such non-events the rainfall characteristics were retained so that the trigger for runoff initiation could be examined.

The characteristics of storms that do and do not cause a runoff event can best be distinguished by means of logistic regression. Logistic regression is the most appropriate technique for predicting a binary outcome (flow event vs. non flow event) from continuous explanatory variables (e.g. antecedent drain flow). This method transforms from a probability scale (0, 1) to the scale of continuous variables (∞, -∞). The transformation used is the logit transform, $y=log(\Theta/(1-\Theta))$ where Θ is the probability of a flow event occurring. The transformed parameter y can then be linearly related to the chosen explanatory variables such as rainfall intensity or antecedent flow.

This study considers the following characteristics in the analysis (Fig. 4.5):

1. Rainfall character

Each individual rain storm is characterised in terms of its total rainfall (T-mm), duration of the event (D- hours) and peak intensity (I- mm/h). The derived measured are also amalgamated into a single non-dimensional parameter- DI/T. This non-dimensional parameter has been successfully used by Heppell et al. (2002) and can be considered the ratio of the peak to the average intensity.

2. Antecedent flow character

The pre-existing condition of the ground on to which any precipitation falls is characterised by discharge of the drain in the time slot prior to the start of the rainfall event.

3. Time since previous rainfall event

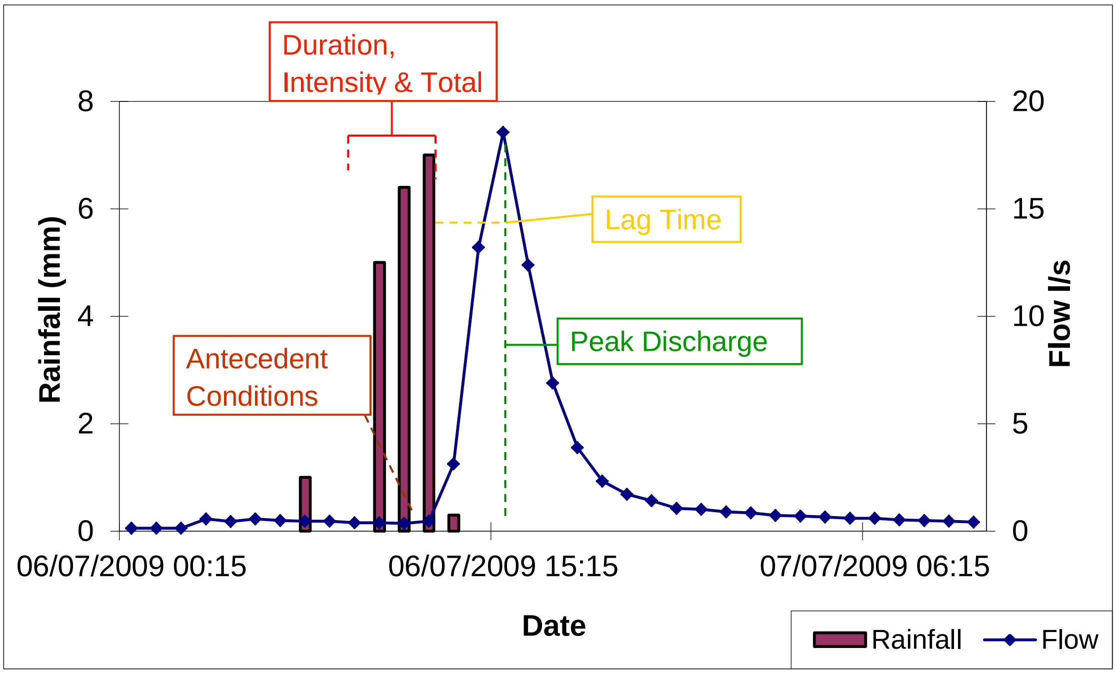


Fig. 4.5: Deconstruction of hydrograph for event analysis.

The logistic regression models were fitted using forward and backward selection procedures for the explanatory variable in order to find the best-fit model based on a minimum number of significant variables: significance was considered acceptable at the 95% probability level or above. Although significance of parameters was the priority for inclusion, improved concordance of the model with the data was also considered. Within any fitted logistic model the odds ratio of a variable is considered as a measure of its importance of that variable relative to other variables in the fitted model. The odds ratio is a measure of effect size, describing the strength of association or non- independence between two binary data values. The higher the odds ratio, the greater the variable's importance in the model. The odds ratio was used to establish which of the variables was the predominant control in determining whether a flow event was likely to occur or not.

The process of event analysis is limited by the subjective method by which the rainfall events are selected for analysis. Although care was taken to ensure that all separate rainfall events were considered, quite often these rainfall events were followed by multiple flow peaks. If the rainfall event could not be unambiguously matched to the correct subsequent flow event then the event was not recorded in the event analysis. Also precipitation events which consisted of snow or when snow was on the ground had to be discounted as the snow interfered with the lag between input and possible output. However, the overall effect of these limitations is considered to be small due to the large number of events that were analysed successfully.

4.4 Results

4.4.1 Water Table

Observations of water table depth have been made during the pre and post blocking period with a total of 1860 observations being recorded. A small mean decrease of 1.1cm in the depth to the water table from 6cm to 5cm can be seen in the experimental catchment on Cronkley Fell post blocking, i.e. water tables did move nearer the surface upon blocking (Fig. 4.6). Although this rise is very small it is statistically significant and may reflect the naturally wet nature of the site. The average water table prior to blocking is close to the peat surface anyway which means that the capacity for the peat to take in additional water is small so the effect on the water table would in turn be small. Interestingly the water table at the pristine catchment, where drainage has not occurred is lower than that of the control and experimental catchment on Cronkley Fell. The site at Atkinson Moss is naturally drier and it is important to consider the natural character of any site when assessing the impact of drain blocking on the hydrology.

ANOVA was performed on the raw water table data from Cronkley Fell and Atkinson Moss and it was found that month of the year and blocking are significant factors at the 95% probability (Table 4.1). The month factor explains the majority of the variance in the dataset but the error term still explains 68.9% of the variance of the water table. The significance of the month reflects the seasonal variation in the water table with higher water tables being recorded in the winter and lower water tables during the drier summer. The interaction between month and blocking was also considered in the ANOVA but was found to be statistically insignificant. This indicates that the effects of drain blocking in the study catchment on the water table appear to be immediate and do not take time to gradually build up post blocking.

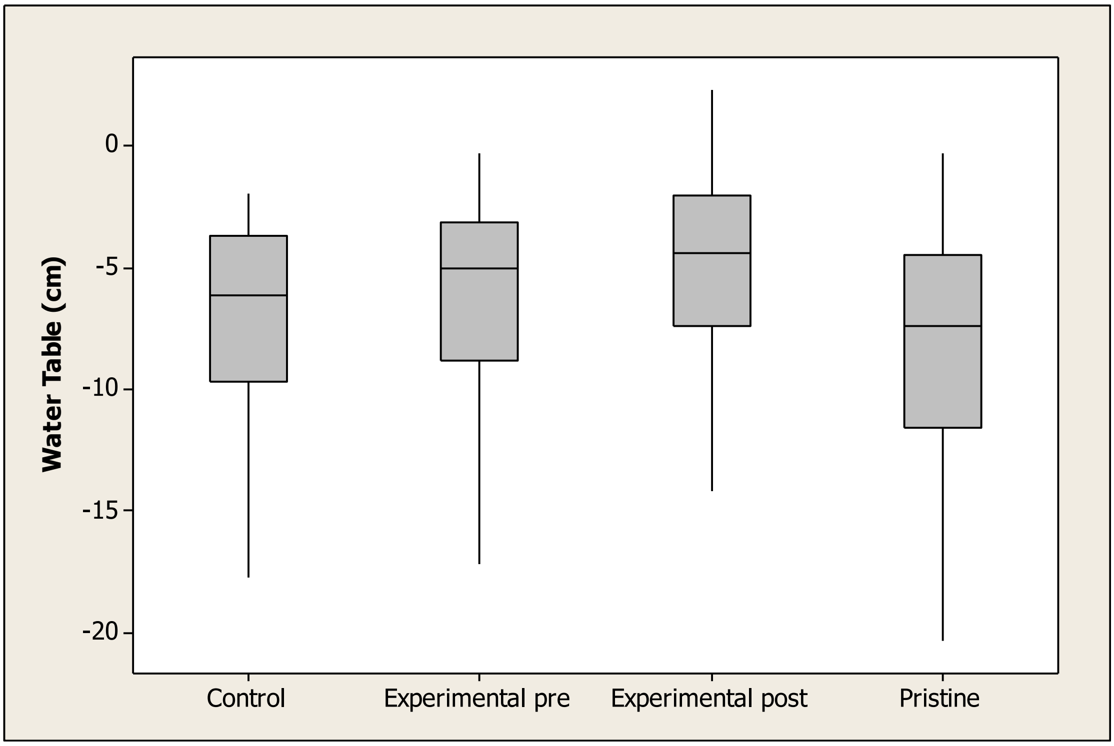


Fig. 4.6: Depth of the water table for the control catchment and the experimental catchment on Cronkley Fell and the pristine catchment at Atkinson Moss. Control n=930, Experimental pre n=465, Experimental post n=465.

Factor	P	Proportion of variance (%)
Month	<0.001	27.3
Blocking	<0.001	3.8
Month x Blocking	>0.5	
Error		68.9

Table 4.1: ANOVA of water table for all monitored sites and months giving the probability of the factor/interaction and the proportion of the variance explained by the factor.

The comparison of relative water table shows a similar pattern with a statistically significant yet very small rise in the water table of 3.4% (Fig. 4.7). The majority of the values of relative water table are under -1. This indicates that the water table at the experimental catchment is lower than at the control catchment with -1 representing the unblocked control catchment to which the experimental catchment is being compared.

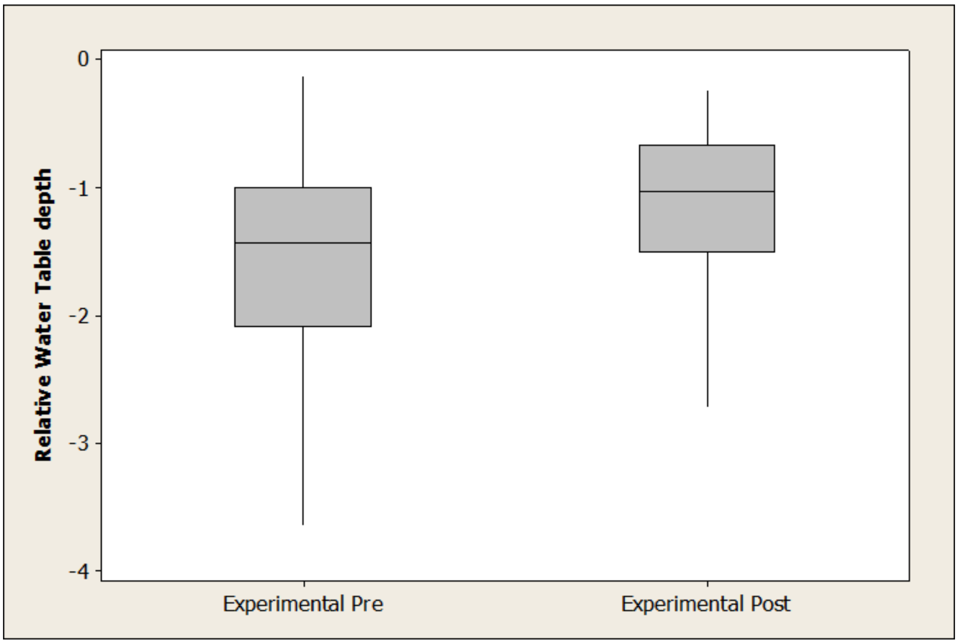


Fig. 4.7: The relative depth of the water table for the experimental catchment when compared to the control catchment on Cronkley Fell in the pre and post blocking period. Experimental pre, n=465; Experimental post n=465.

ANOVA was again performed on the relative water table depth data with similar results to that carried out on the raw water table depth values (Table 4.2). Month and blocking were found to be significant with the error explaining the majority of the variance in the data. As discussed above the site at Cronkley Fell was naturally very wet to start with so a large shift in the water table would be unexpected as the site has little capacity to take in additional water.

Factor	P	Proportion of variance (%)
Month	<0.001	28.4
Blocking	<0.001	0.7
Month x Blocking	>0.5	
Error		70.9

Table 4.2: ANOVA of the relative water table giving the probability of the factor/interaction and the proportion of the variance explained by the factor.

Spatial analysis of the water table was performed in order to assess whether the recorded water table depth is seen to vary with slope position and with proximity to a drain and whether this is seen to change post blocking. Analysis of the spatial variation of the water table (Fig. 4.8, 4.9 and 4.10) indicates that in the control catchment and the experimental catchment both in the pre and post blocking period the distribution of the water table is quite random. The data shows no systematic pattern with the water table not being higher or lower nearer the drains. Also there is no apparent change in water table downslope. This random pattern in water table distribution continues post blocking (Fig 4.11).

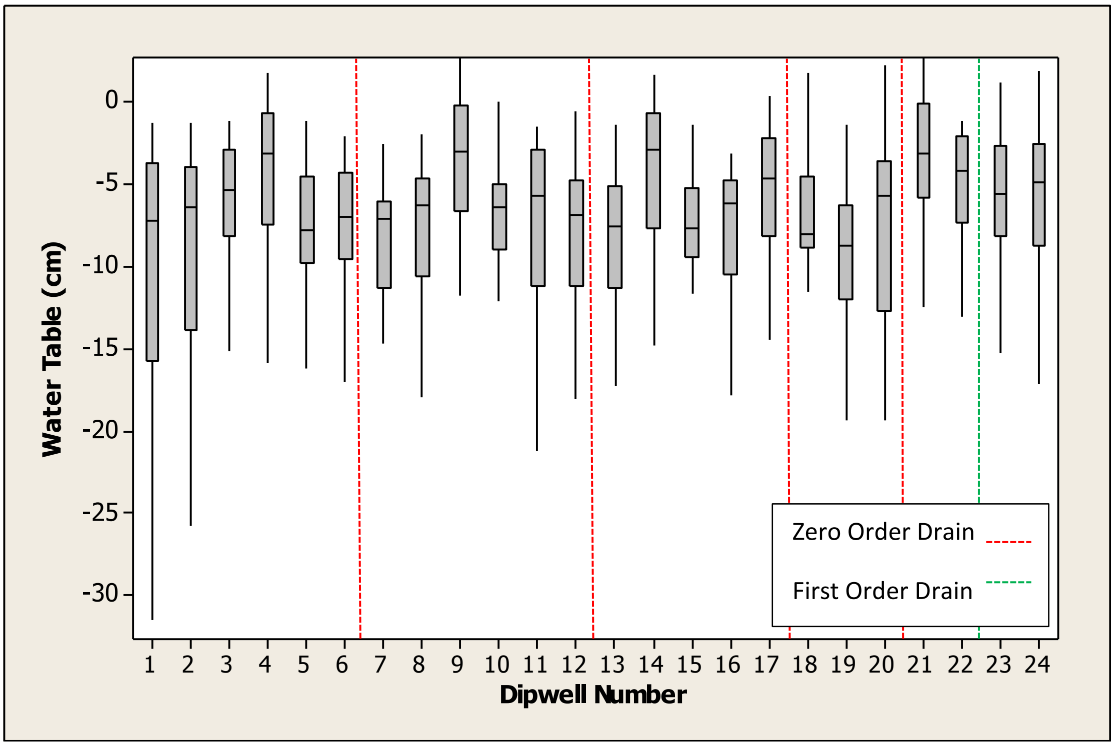


Fig. 4.8: The spatial analysis of individual dipwells for the control catchment on Cronkley Fell

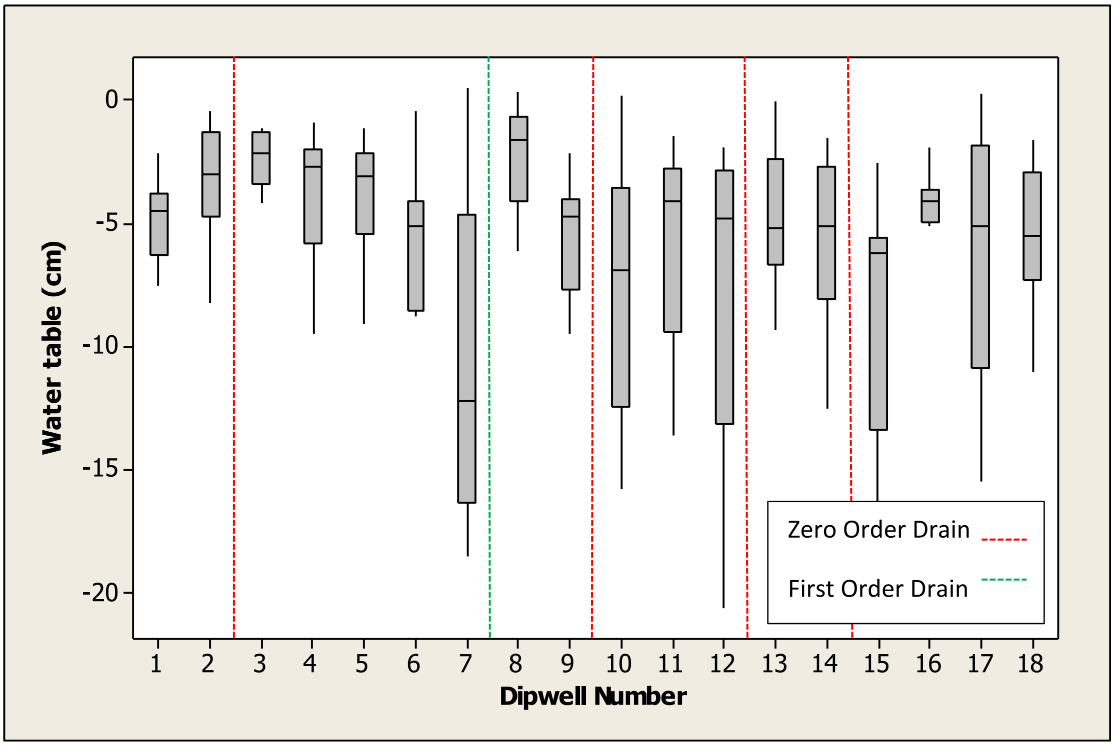


Fig. 4.9: The spatial analysis of individual dipwells for the experimental catchment on Cronkley Fell in the pre blocking period.

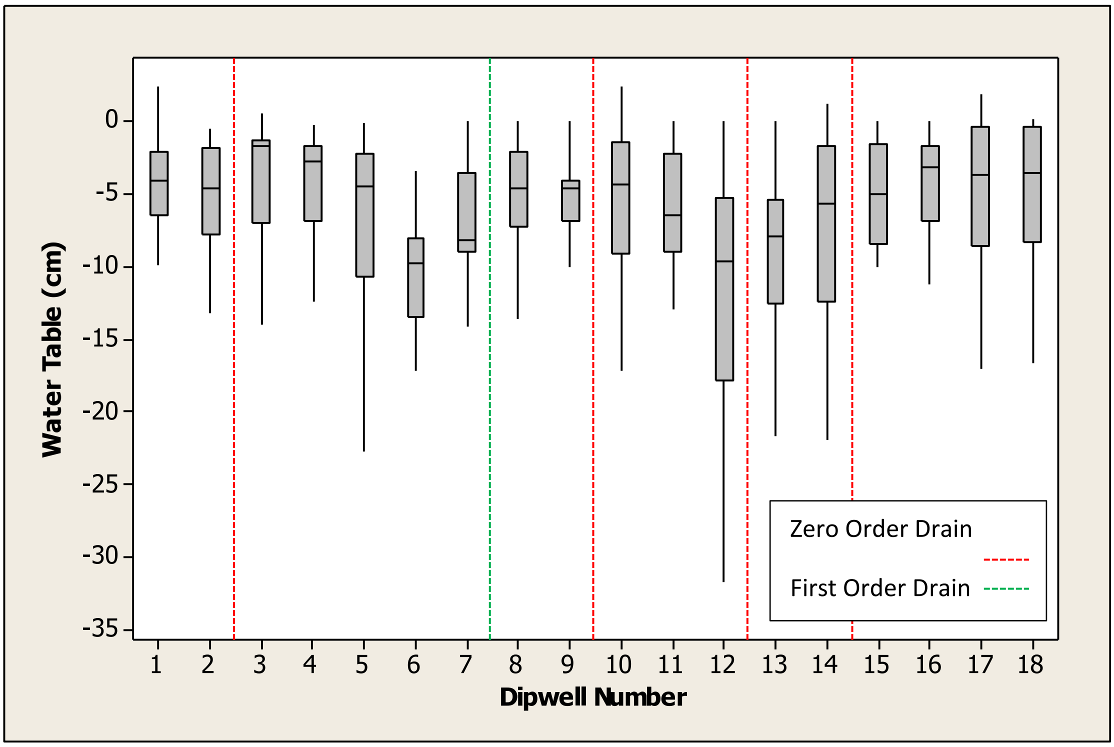


Fig. 4.10: The spatial analysis of individual dipwells for the experimental catchment in the post blocking period.

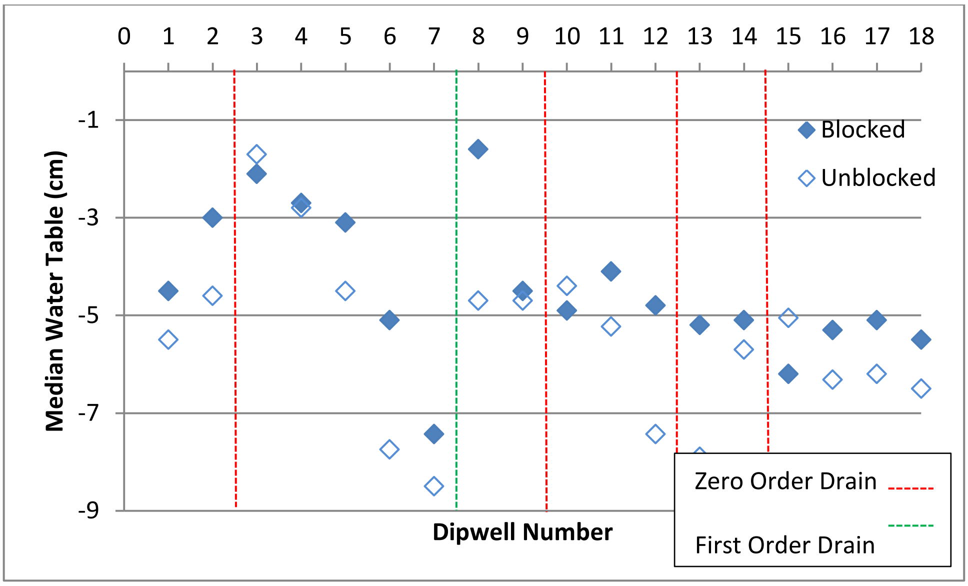


Fig. 4.11: The comparative spatial analysis of individual dipwells for the experimental catchment in the pre and post blocking period.

4.4.2 Drain water yield and export

Despite the relatively small change in the water table, analysis of average monthly drain water yield showed a considerably larger decrease post blocking. In the control catchment water yield was seen to increase from zero to first order (Fig. 4.12). This is to be expected as the first order drains are natural larger. When the values of monthly water yield are examined for the experimental catchment for the pre and post blocking years at the zero and first order scale the water yield of the blocked drains is seen to decrease by a mean value of 16% on the zero order drains and 12% on the first order drains (Fig. 4.13).

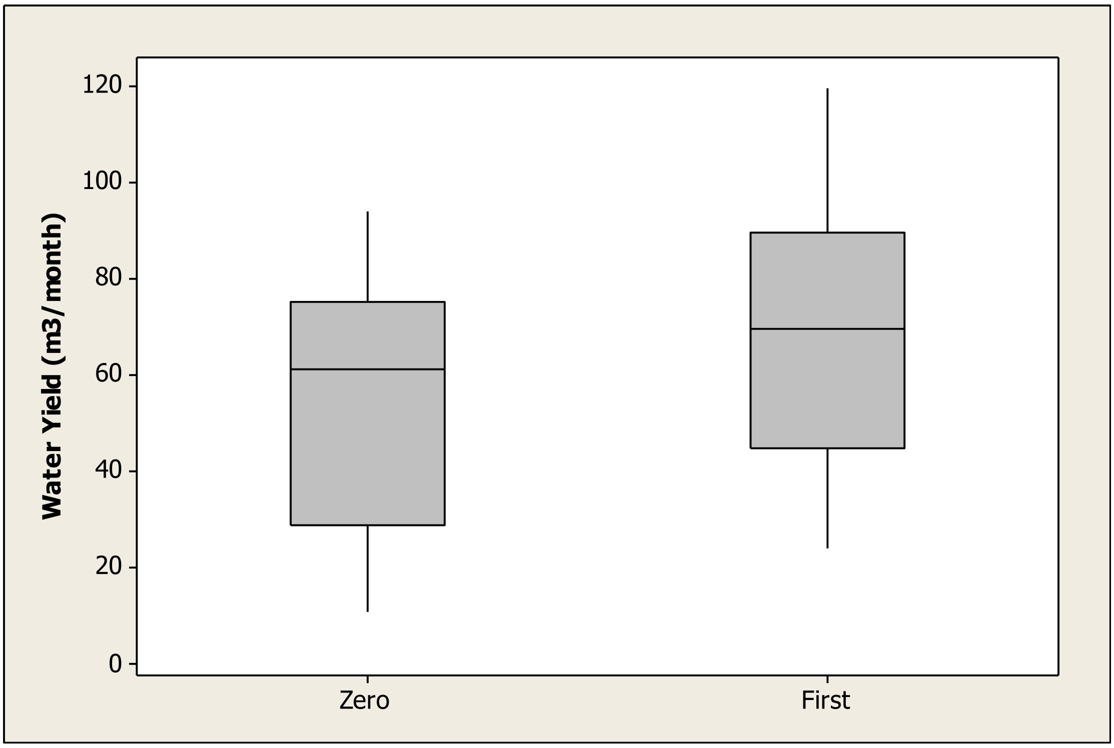


Fig. 4.12: The water yield for the zero and first order drains at the control catchment on Cronkley Fell

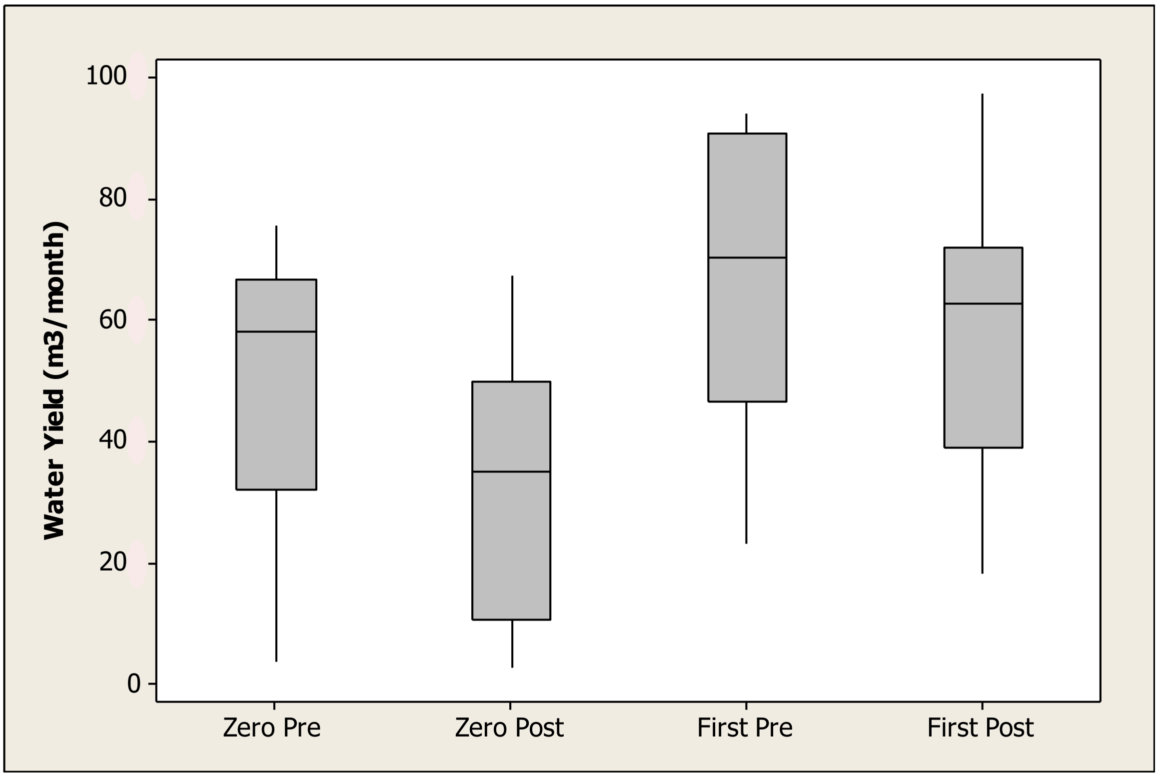


Fig. 4.13: The water yield for the zero and first order drains at the experimental catchment in the pre and post blocking period on Cronkley Fell

ANOVA was performed on the monthly water yield values from Cronkley and it was found that scale, month of the year, blocking and the interaction between blocking and scale were significant factors at the 95% probability (Table 4.3). The scale factor explains the majority of the variance in the dataset but the error term still explains 19.2% of the variance of the water yield. The significance of scale reflects how the drains increase in size as water travels down the catchment. The water yield is affected by seasonal changes with some months being wetter than others reflecting the significance of the month factor in the ANOVA. Blocking is found to have a significant impact on water yield with the blockages slowing the movement of water through the catchment forcing it to take alternative pathways. The significance of the interaction between scale and blocking reflects how the size of the water yield reduction reduces as scale increases agreeing with what was inferred from Figure 4.13. The ANOVA also considered the interaction between month and blocking. Similarly to the water table data the interaction between month and blocking was found to be insignificant indicating an immediate effect of blocking rather than a gradual cumulative effect.

Factor	P	Proportion of variance (%)
Scale	<0.001	29.3
Month	<0.001	25.2
Blocking	<0.001	17.6
Blocking x Scale	<0.001	8.7
Month x Blocking	>0.5	
Month x Scale	>0.5	
Error		19.2

Table 4.3: ANOVA of monthly water yield giving the probability of the factor/interaction and the proportion of the variance explained by the factor.

In order to negate the effect of natural year on year variation in drain discharge the water yield in the experimental catchment was considered relative to the water yield in the control catchment. When relative water yield is examined a similar decrease in water yield upon blocking is observed (Fig 4.14). A decrease in relative water yield upon blocking of 14% is recorded at the zero order scale and 8% at the first order.

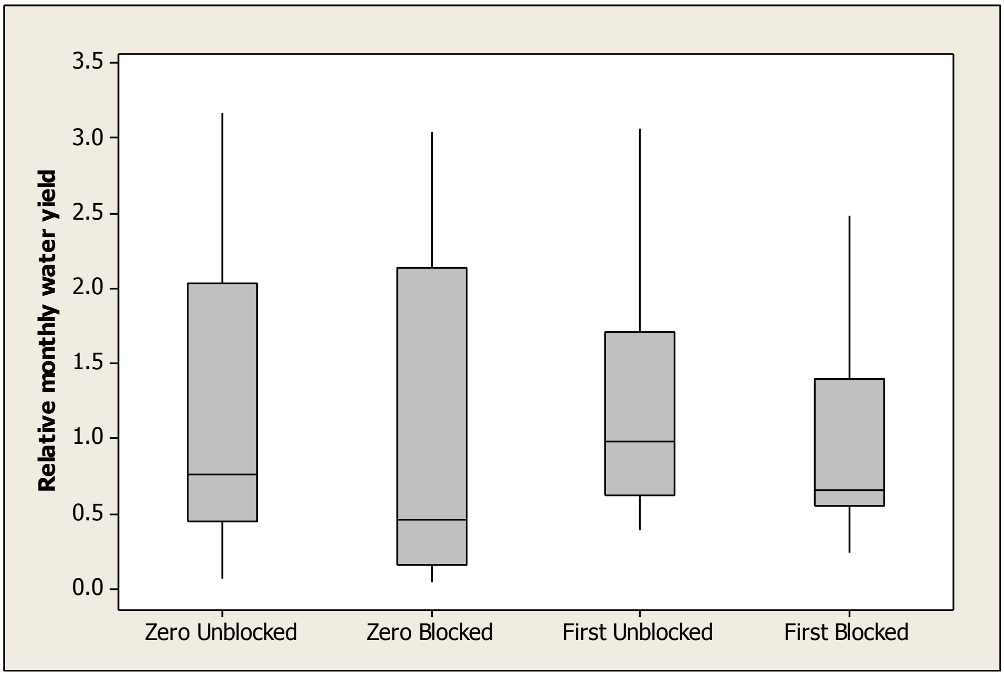


Fig. 4.14: The relative monthly water yield for the zero and first order drains at the experimental catchment on Cronkley Fell for the pre and post blocking period.

ANOVA was performed again this time on the relative water yield values from Cronkley and it was found that scale, month of the year, blocking and the interaction between blocking and scale were significant factors at the 95% probability (Table 4.4). The scale factor explains the majority of the variance in the dataset but the error term still explains 24.6% of the variance of the water yield. The significance of scale and month again reflect the increase in drain size and seasonal variation with the significance of blocking reflecting the reduction in relative water yield after the drain has been dammed. The ANOVA again found that the interaction between blocking and scale is significant with the reduction in relative water yield changing with scale.

Factor	P	Proportion of variance (%)
Scale	<0.001	25.3
Month	<0.001	24.2
Blocking	<0.001	20.6
Blocking x scale	<0.001	5.3
Month x Blocking	>0.5	
Month x scale	>0.5	
Error		24.6

Table 4.4: ANOVA of relative monthly water yield giving the probability of the factor/interaction and the proportion of the variance explained by the factor.

As discussed above the water yield will naturally increase with scale as the drains become increasingly larger. In order to establish whether the effects of scale on the water yield are due to this natural increase in drain size or due to the effect of drain blocking similar analysis was performed on the monthly water export from the area. Water export is defined as the water yield per unit area.

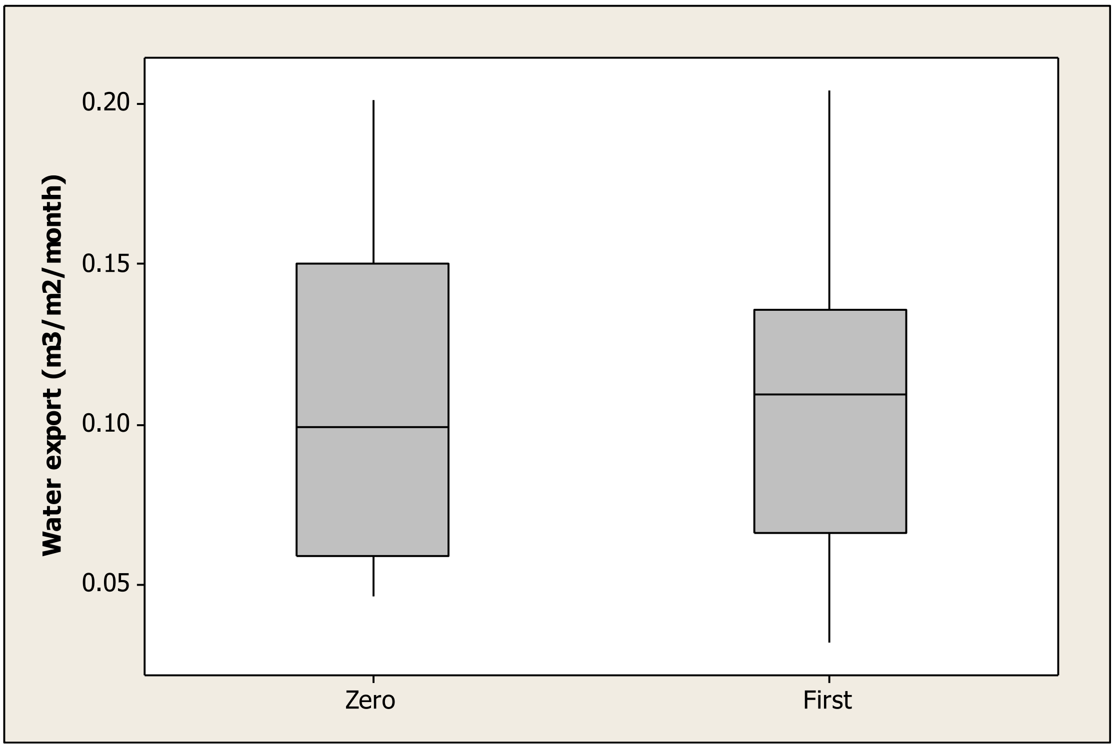


Fig. 4.15: The water export for the zero and first order drains at the control catchment on Cronkley Fell

The comparison of the zero order and first order monthly water export values for the control catchment on Cronkley Fell (Fig. 4.15) shows that water export increases slightly up scale. The increase in water export with scale is considerably less than what was indicated from the water yield data (Fig. 4.12) and demonstrates how the natural increase in the amount of water in the system simply due to an increase in drain size has to some extent been negated. Despite the negation of this natural scale effect a small mean increase of 0.7% is still recorded from zero to first order drain suggesting water may be being added to the system from an alternative source.

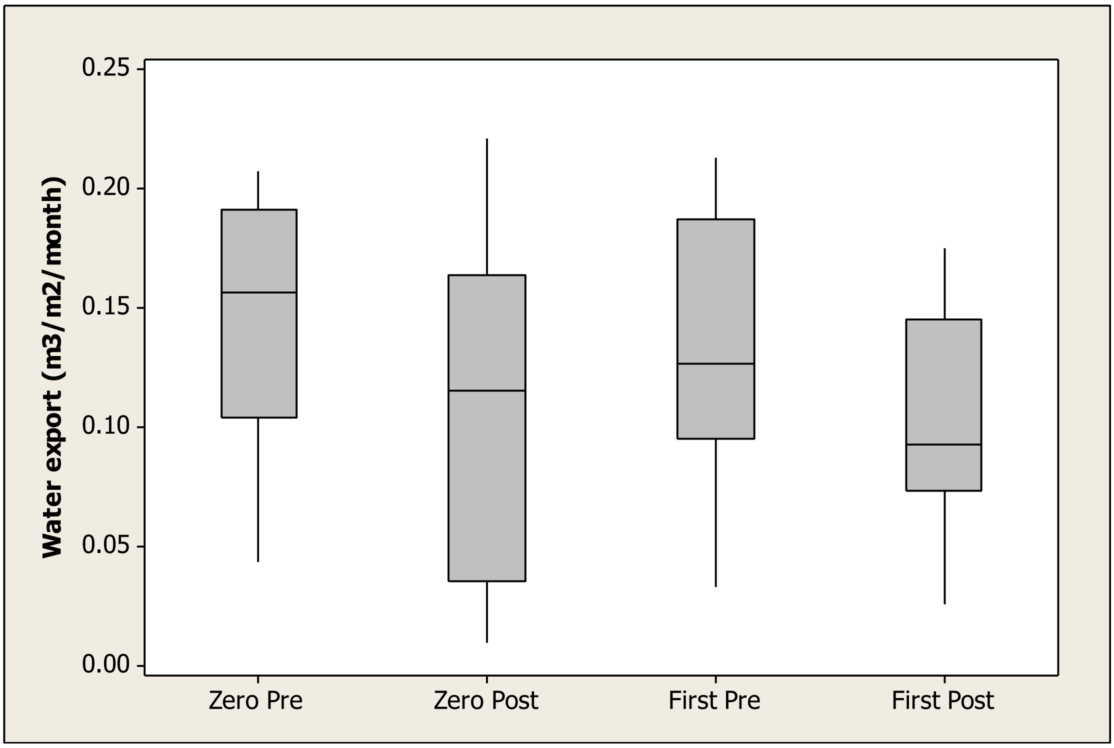


Fig. 4.16: The water export for the zero and first order drains at the experimental catchment on Cronkley Fell for the pre and post blocking periods

The comparison of the zero and first order drain water export data for the pre and post blocking period on the experimental catchment demonstrates a decrease in water export upon blocking (Fig. 4.16). However this reduction is seen to decrease upscale as was indicated by the water yield data. At the zero order scale a reduction in water export of 13% is recorded and at the first order scale 11%. The size of the decrease in water export reduction upscale is however smaller when the amount of water passing through the drain is considered as water export rather than water yield. This reflects again how the water export parameter has a negating influence on the natural increase in discharge with scale. Despite this a decrease in water export reduction is still observed upscale giving evidence for the bypassing of water around the drain blocks.

The water export data was subjected to a process of ANOVA. It was found that month of the year, blocking, scale and the interaction between blocking and scale were significant factors at the 95% probability (Table 4.5). The month factor explains the majority of the variance in the dataset but the error term still explains 34.4% of the variance of the water export. The significance of month again reflect the seasonal variation in water export with the significance of blocking reflecting the reduction in water export after the drain has been dammed. Scale is found to be significant albeit to a reduced extent compared to when ANOVA was performed on the water yield data. This reflects how despite the water export factor being independent of scale an increase in water export is still found suggesting additional water is being added to the system from external sources. The ANOVA again found that the interaction between blocking and scale is significant reflecting how the reduction in water export upon blocking varies with increasing scale.

Factor	P	Proportion of variance (%)
Month	<0.001	28.3
Blocking	<0.001	25.1
Scale	<0.001	8.3
Blocking x Scale	<0.001	4.2
Month x Blocking	>0.5	
Month x Scale	>0.5	
Error		34.4

Table 4.5: ANOVA of monthly water export giving the probability of the factor/interaction and the proportion of the variance explained by the factor.

In order to negate the effect of natural year on year variation in drain water export the water export in the experimental catchment was considered relative to the water export in the control catchment. When relative water export is examined a similar decrease in water export upon blocking is observed (Fig 4.17). A decrease in relative water export upon blocking of 10% is recorded at the zero order scale and 7.5% at the first order. The size of this decrease in relative water export is again seen to reduce upscale although the difference in the size of the reductions at the zero and first order drains is smaller reflecting the independence of the water export variable from scale.

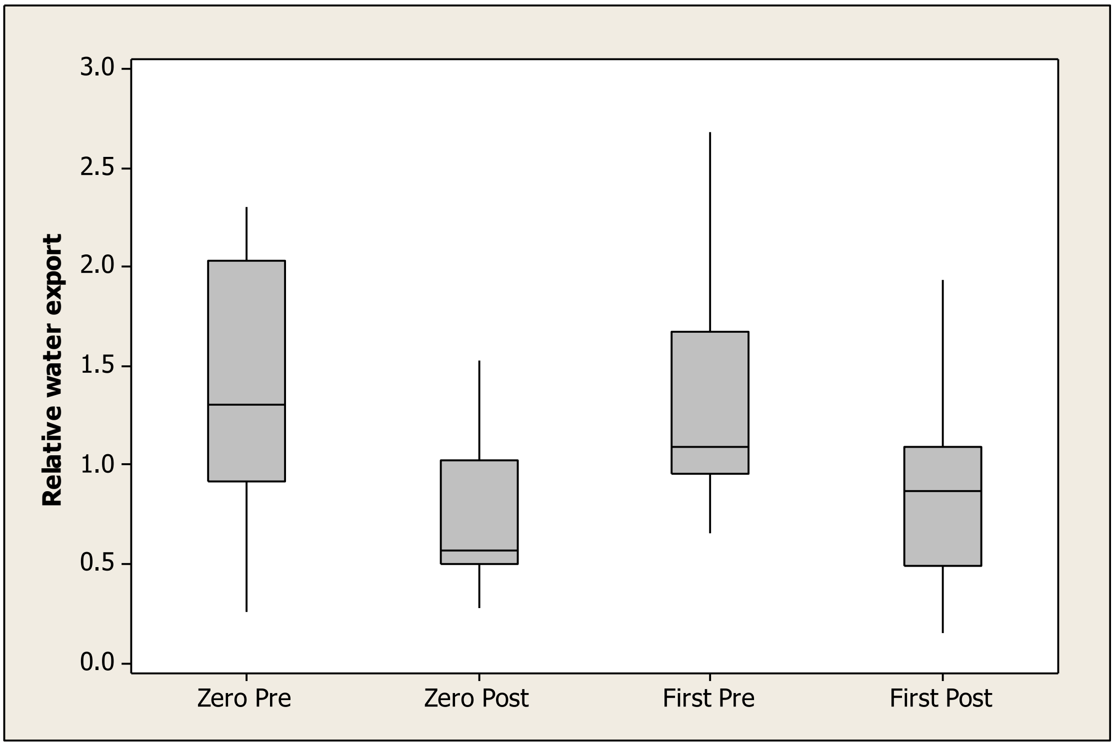


Fig. 4.17: The relative monthly water export for the zero and first order drains at the experimental catchment on Cronkley Fell in the pre and post blocking period.

ANOVA was performed again this time on the relative water export values from Cronkley and it was found, similar to water export, in that month of the year, blocking, scale and the interaction between blocking and scale were significant factors at the 95% probability (Table 4.6). The month factor explains the majority of the variance in the dataset but the error term still explains 20.1% of the variance of the relative water export. The significance of month again reflect the seasonal variation in relative water export with the significance of blocking reflecting the reduction in relative water export after the drain has been dammed. The ANOVA again found that the interaction between blocking and scale is significant with the reduction in relative water export changing with scale.

Factor	P	Proportion of variance (%)
Month	<0.001	33.2
Blocking	<0.001	27.3
Scale	<0.001	10.2
Blocking x Scale	<0.001	9.2
Month x Blocking	>0.5	
Month x Scale	>0.5	
Error		20.1

Table 4.6: ANOVA of monthly relative water export giving the probability of the factor/interaction and the proportion of the variance explained by the factor.

A reduction in both water yield and export has been found post blocking. However with a reduction in water yield and export of the size recorded, a larger decrease in water table depth would be expected indicating that water is being removed from the system in other ways. Water may be being lost from the system by increased evapo-transpiration also it is possible that the shape and size of the catchment has changed post blocking as water which would have previously exited the catchment via the drains now finds alternative pathways from the system.

4.4.3 Surface runoff

The presence of surface runoff was determined by whether water was found in crest fall run off traps distributed above and below a drain on Cronkley Fell (section-4.3.1). The runoff traps were checked for the presence of water on a total of 24 field visits on the control catchment and 22 visit on the experimental (10 visits pre blocking and 12 post blocking). On the control catchment this gave a potential total of 384 readings upslope of the drain and 384 downslope the drain. For the experimental catchment pre blocking a potential total of 100 measurements were made upslope the drain and 50 downslope, post blocking 120 measurements were made upslope the drain and 60 downslope.

	Control	*Experimental*
Pre blocking (upslope)	136 (36%)	29 (29%)
Post blocking (upslope)		49 (41%)
Pre blocking (downslope)	103 (27%)	15 (31%)
Post blocking (downslope)		22 (37%)

Table 4.7 The number of runoff events recorded for the control and experimental catchment on Cronkley Fell. The value in brackets is the number of runoff events as a percentage of the total number of possible readings.

The proportional analysis on the data collected from the runoff traps indicates a slight increase in surface runoff post blocking (Table 4.7). Post blocking above the drain on the experimental catchment the number of runoff traps with water found inside has increased from 29% of the total number of traps to 41%. Below the drain a similar increase is recorded from 31% pre blocking to 37% post blocking. The movement of water through the system is being slowed as it is held back by the blockages. The water will not just stay in one place and will attempt to find alternative paths through the catchment such as by surface runoff.

4.4.4 Catchment hydrograph

Examination of the control catchment hydrographs demonstrated the flashy nature of the system with rainfall events quickly moving down the catchment due to the low storage capacity of the nearly saturated peat bog (Fig. 4.18). Examination of events during low flow conditions showed changes in the level of the baseline flow from zero to first order streams (Fig. 4.19). Low flow conditions are defined as those where a rainfall has not occurred for a considerable time before the examined flow period thus the flow in the drain is exceptionally small and the drain is on the point of no recordable flow. During relative dry periods flow in the zero order feeder drains would cease yet at the first order scale flow was still measurable. The presence of continued flow at this scale demonstrates the open nature of the system. The water present at the first order monitoring site is likely to be a mixture of water from the feeder zero order drains and other sources within the catchment such as runoff or soil water. The continuation of measurable flow during drier conditions would also explain why export of DOC is seen to increase with scale despite the only slight changes in concentration.

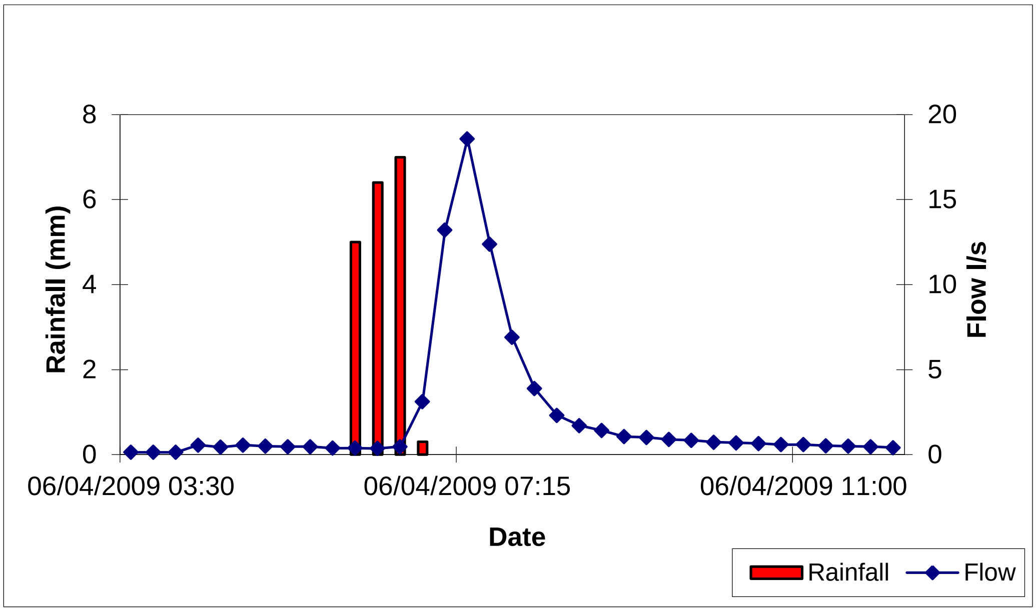


Fig. 4.18: Example hydrograph from the control catchment demonstrating the flashy nature of the hydrology. A rainfall event is recorded which is followed quickly be an increase in flow that is of a short duration.

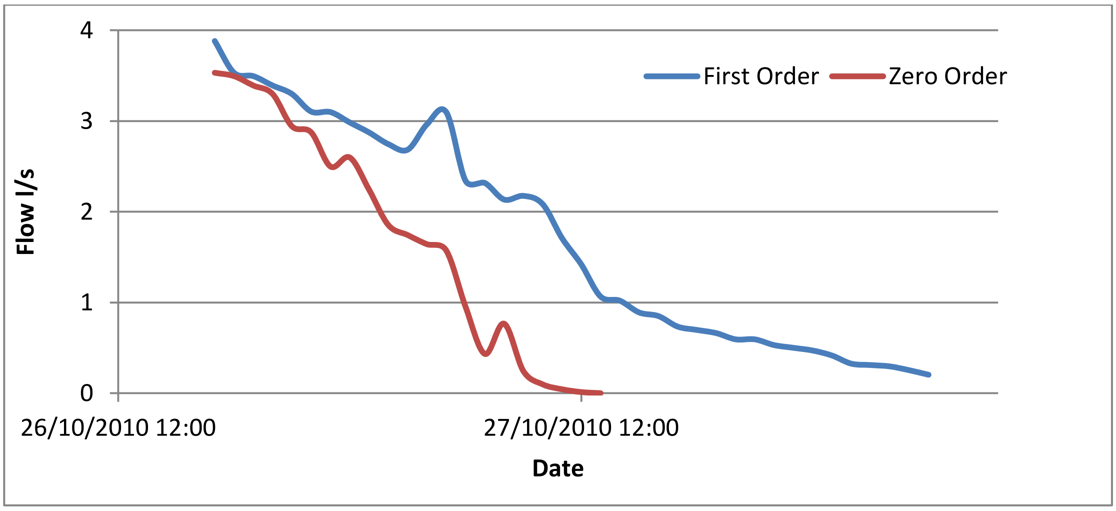


Fig. 4.19: Example of a low flow event from the control catchment. During dry period flow is seen to continue for a longer period on the first order drain than the zero order drain

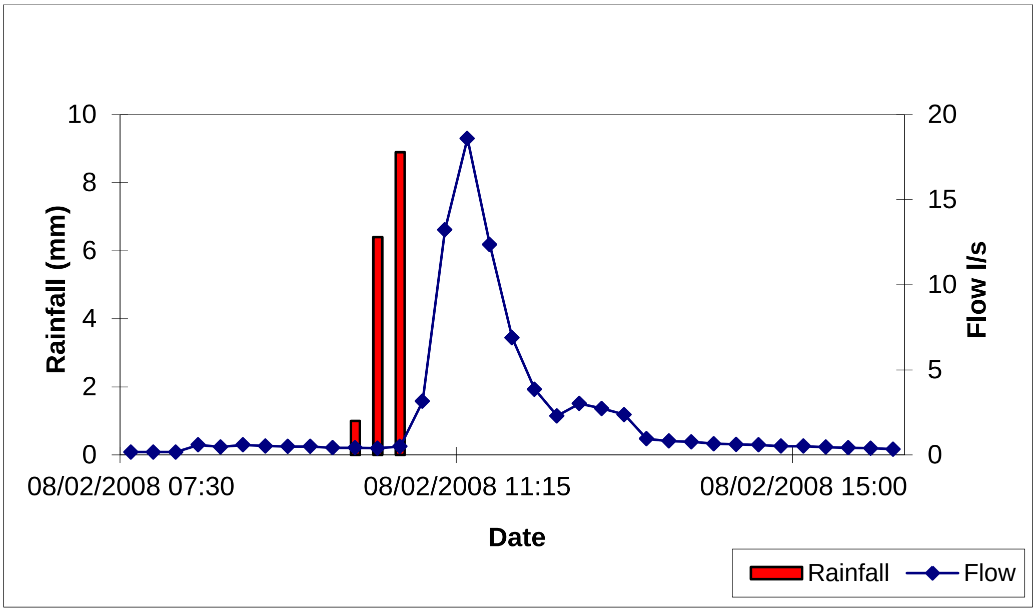


Fig. 4.20: Example hydrograph from the experimental catchment demonstrating the flashy nature of the hydrology. A rainfall event is recorded which is followed quickly be an increase in flow that is of a short duration.

The analysis of the hydrographs in the experimental catchment pre blocking shows a similar pattern to those in the control. The catchment as a whole has a flashy nature (Fig. 4.20) with a tendency for flow to continue in dry conditions at the first order scale when the zero order drains have run dry (Fig. 4.21). Post blocking the shape of the hydrograph for both zero and first order drains in the experimental catchment is seen to change post blocking with peak flows being on average 13% smaller but of average 30 minute longer duration (Fig. 4.22). However, this change is less marked on first order drains which suggests that an element of bypass flow is occurring adding additional water and possible DOC at this scale. Low to moderate rainfall events are seen to take longer to move through the catchment.

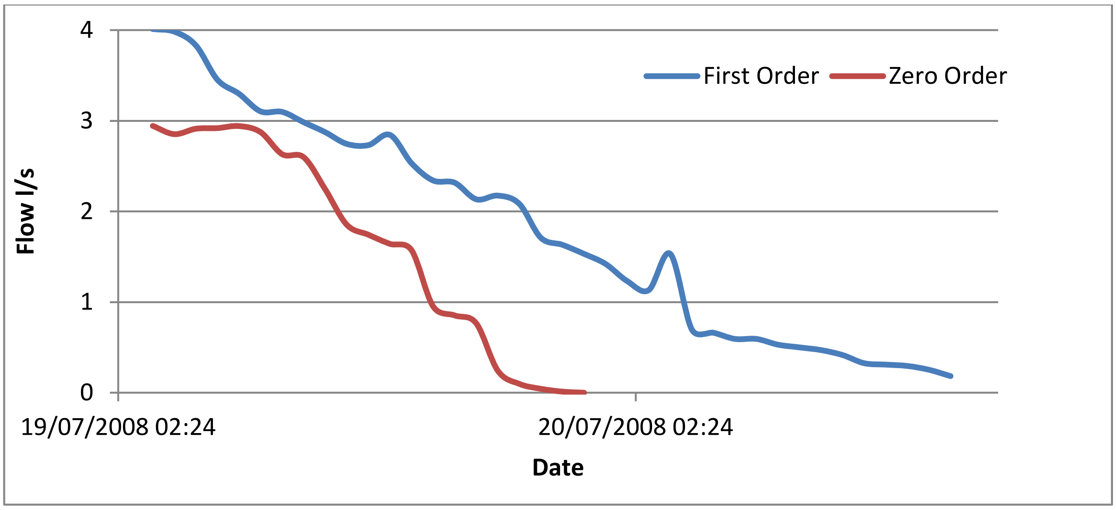


Fig. 4.21: Example of a low flow event from the experimental catchment. During dry period flow is seen to continue for a longer period on the first order drain than the zero order drain

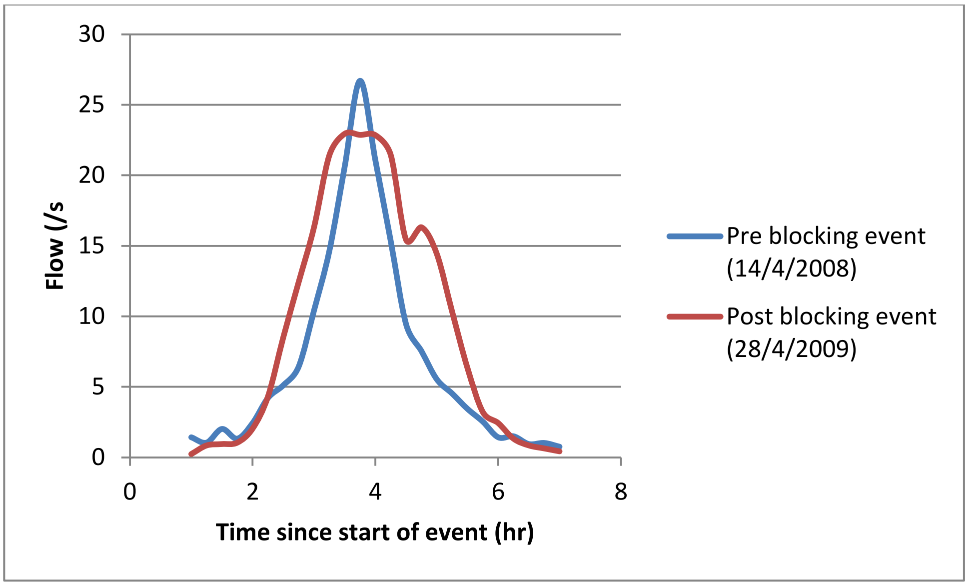


Fig 4.22: The effect of blocking on the shape of the hydrograph for a zero order drain on the experimental catchment on Cronkley Fell.

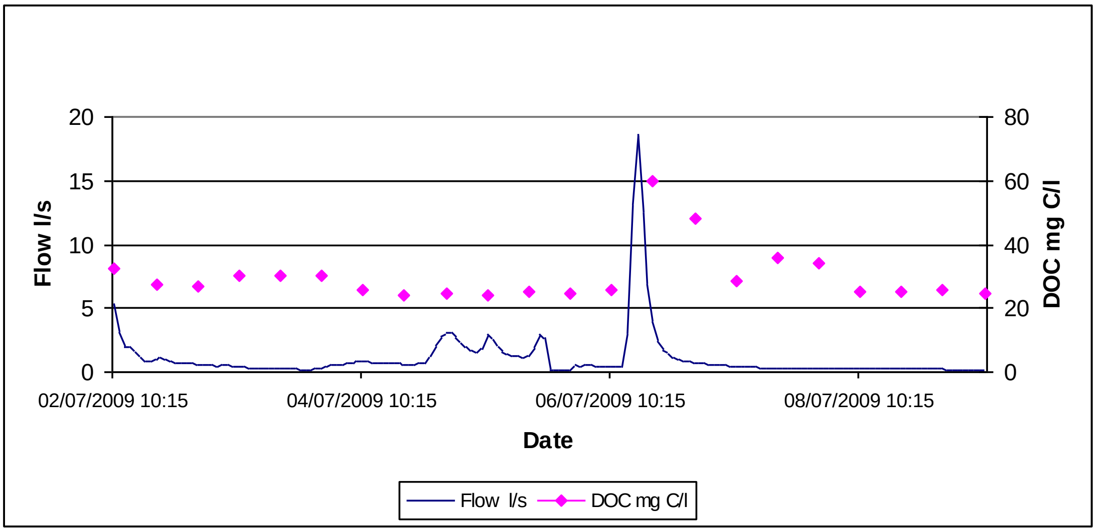


Fig. 4.23: Effect of high intensity rainfall and flow event on DOC concentration in the first order experimental drain post blocking.

Despite a reduction in the flow peak following blocking, a tipping point is visible during very high intensity rainfall events where flow peaks in both blocked zero and first order drains are unusually high for a shorter period of time (Fig. 4.23). During these events water is seen to flow over blockages and via surface runoff to enter the drains causing the short term high flow conditions. These events are also associated with higher than average DOC concentrations when compared to average DOC levels post blocking or the DOC levels recorded in the unblocked catchment. Post blocking, water is held back in the peat, leading to higher DOC concentrations in the soil such that when these high intensity rainfall events occur the DOC is flushed from the system causing high levels of DOC concentration in the drains.

4.4.5 Event Analysis

All rainfall and runoff events analysed were subjected to a process of binary logistic regression. A total of 2013 rainfall events were analysed. Of these events 60% (1207 rainfall events) could be associated with a measurable flow event. The remaining 40% (806 rainfall events) were classified as non-events with no identifiable flow event being recorded after the rainfall event. A qualitative description of the analysed rainfall and flow events can be found in Table 4.8.

Descriptor	***Control***		***Experimental***	
	Max	***Min***	***Max***	***Min***
Rainfall duration (h)	28.8	0.2	28.8	0.2
Total rainfall (mm)	34.0	0.2	34.0	0.2
Peak rainfall intensity (mm/h)	25.6	0.08	25.6	0.08
DI/T	40.96	1.0	40.96	1.0
Initial flow (l/s)	1.13	0	0.25	0
Flow change (l/s)	5.21	0.02	4.73	0.02

Table 4.8: Qualitative description of recorded rainfall and flow events

The use of logistic regression on all the events from both sites gives the following best-fit equation (Eq1). Only those variables significant at the 95% level were included.

$$\ln\left(\frac{\theta}{1-\theta}\right) = -0.11t + 1.66DI/T + 0.88$$

$$n=2013 \qquad (1)$$

Where:

Ɵ = the probability that a flow event will occur during the rainfall event;

t = the time since the last event

DI/T = the dimensionless parameter of rainfall character.

Standard error on the coefficients:

Constant = 0.169 t = 0.006 DI/T = 0.156

The analysis of the odds ratio indicates that the factor controlling whether a flow event is likely to occur after a rainfall event is the characteristics of that rainfall event rather than the time since the previous event i.e. the antecedent conditions of the ground. Equation 1 is 84% concordant with the data. If the individual components of DI/T are included in the logistic regression the following best-fit equation, including only those variables significant at the 95% level, is calculated:

$$\ln\left(\frac{\theta}{1-\theta}\right) = -0.11t + 1.17D + 2.98I - 2.45$$

n=2013 (2)

where:

D = the duration of the rainfall event

I =the intensity.

Standard error on the coefficients:

Constant = 0.309 t = 0.008 D = 0.081 I =0.303

The odds ratio suggests that the most important variable in controlling the probability of a flow event is the intensity of the rainfall event with equation 2 showing a 75% concordance with the data.

When equation 1 is plotted with the data collected from the event analysis of both non flow events and flow events (Fig. 4.24) again the importance of rainfall character is demonstrated in influencing whether a subsequent flow event will occur. As the probability of an event occurring increases the value of the DI/T is seen to increase.

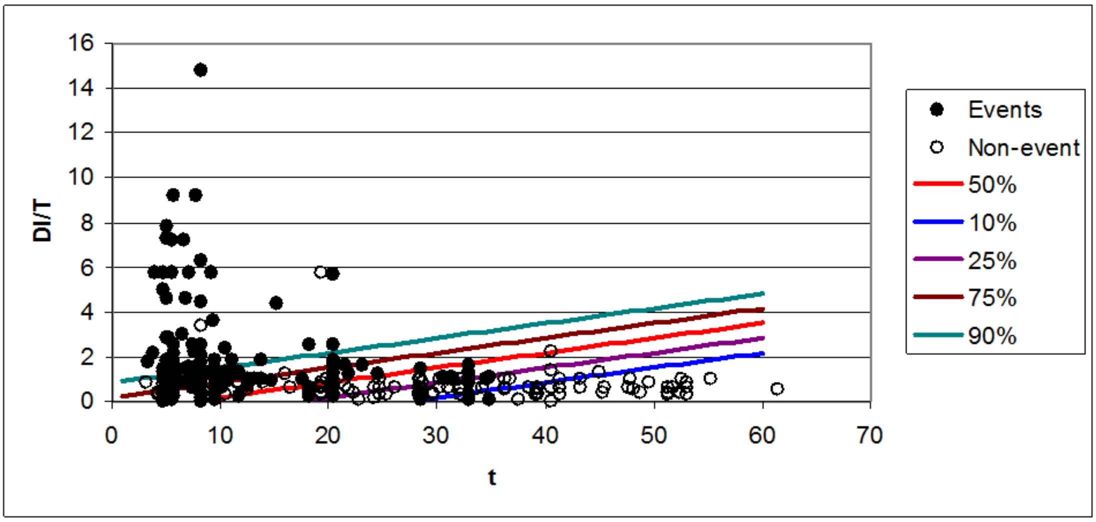


FIG 4.24. The probability of an event occurring based on binary logistic regression of all data from Cronkley Fell using factors DI/T and t.

The presence of a negative value for *t* in equations 1 and 2 is ambiguous as this would indicate that as the time between events decreased the probability of a flow event occurring would also decrease. This is unlikely to be accurate because the closer together the rainfall events are the wetter the peat will be with a lower capacity to store water thus a higher probability of a flow event. This negative value of *t* however is very small with an equally small odds ratio emphasising the negligible influence of the time between events which the logistic regression has found and is most likely a product of measurement error in the field.

The study aims to assess whether the blocking of drains and the increasing scale have an effect on the hydrology of the area. Thus the process of binary logistic regression was performed on the events from each individual catchment at both zero and first order drain scale and in the pre and post blocking period. The control catchment on Cronkley Fell has not been blocked, however the data from the control catchment was analysed in two parts reflecting the pre and post blocking period on the experimental catchment so that any comparisons of hydrology made between the control catchment and the experimental catchment post blocking would reflect changes in the actual water balance rather than any variation in metrological condition between the two years.

Analysis of the events from the control catchment showed that there was no change in influence of controlling factors of flow event probability when moving from the zero to first order drain with analyses from both years producing the same best fit equation, including only those variables significant at the 95%, of:

$$\ln\left(\frac{\theta}{1-\theta}\right) = -0.41t + 0.05DI/T + 5.55$$

Pre blocking zero order n=275
Pre blocking first order n=135
Post blocking zero order n=301
Post blocking first order n= 182 (3)

Standard error on the coefficients:

Constant = 1.028 t = 0.042 DI/T = 0.089

And when DI/T is considered in its constituent parts a best fit equation, including only those variables significant at the 95%, of:

$$\ln\left(\frac{\theta}{1-\theta}\right) = -0.41t + 3.5D + 1.181I + 4.74 \tag{4}$$

Standard error on the coefficients:

Constant = 2.368 t = 0.128 D = 1.091 I = 0.995

The odds ratio for equation 3 indicated again that the DI/T is the most important variable in controlling whether a flow event will occur. Despite the best fit equation for flow events in the control catchment in the pre and post blocking period not changing; the concordance of the data was seen to change with the pre blocking zero order drain recording a concordance of 83%, post blocking zero order, 75%, pre blocking first order, 79%, and post blocking first order, 82%. The odds ratio for equation 4 suggests that the most important variable in controlling the probability of a flow event is again the intensity of the rainfall event with the equation showing a concordance on the pre blocking zero order drain of 76%, post blocking zero order,79%, pre blocking first order, 81%, and post blocking first order, 8%.

Analysis of events from the experimental catchment for the pre blocking year at the zero and first order scale produced the same best fit equation as the data from the control catchment (Equation 3 and 4; pre blocking zero order n=268, pre blocking first order n=136) again indicating that the change in scale from zero to first order drain appears to have little effect on the probability of a flow event occurring. The odds ratio again found DI/T and rainfall intensity to be the most important variables controlling whether a flow event is likely to occur or not with a concordance of 85% for the experimental zero order drain pre blocking and 74% for the experimental first order drain pre blocking. However a change can be seen after the drains have been blocked with both the zero and first order drain in the post blocking period on the experimental catchment producing a best fit equation of:

$$\ln\left(\frac{\theta}{1-\theta}\right) = -0.08t + 4.85DI/T - 2.68 \tag{5}$$

Post blocking zero order n= 136

Post blocking first order n= 271

Standard error on the coefficients:

Constant = 0.416 t = 0.015 DI/T = 0.487

and;

$$\ln\left(\frac{\theta}{1-\theta}\right) = -0.07t + 1.07D + 3.841I - 4.61 \tag{6}$$

Standard error on the coefficients:

Constant = 0.881 t = 0.016 D = 0.520 I = 2.007

The odds ratio for equation 5 indicates that DI/T is the most important variable in controlling the probability of a flow event occurring with an 82% concordance with the data from the zero order drain post blocking and an 80% concordance with the data from the first order drain post blocking. The odds ratio for equation 6 indicates that when the rainfall characteristics are examined as their own entities rainfall intensity is considered the most important variable in controlling whether a flow event is likely to occur with a concordance value of 79% for the data from the zero order drain post blocking and 69% for the first order drain post blocking.

The odds ratios from the pre and post blocking period on the experimental catchment indicate that after the drains have been blocked the characteristics of the rainfall events have an even larger control on the probability of a flow event occurring. However the analysis does indicate that it is the intensity of these rainfall events which becomes more important post blocking rather than the duration of these events. When this data is examined at a 50% probability level (Fig. 4.25) a shift in the 50% probability curve is obvious from the pre to post blocking year on the experimental catchment.

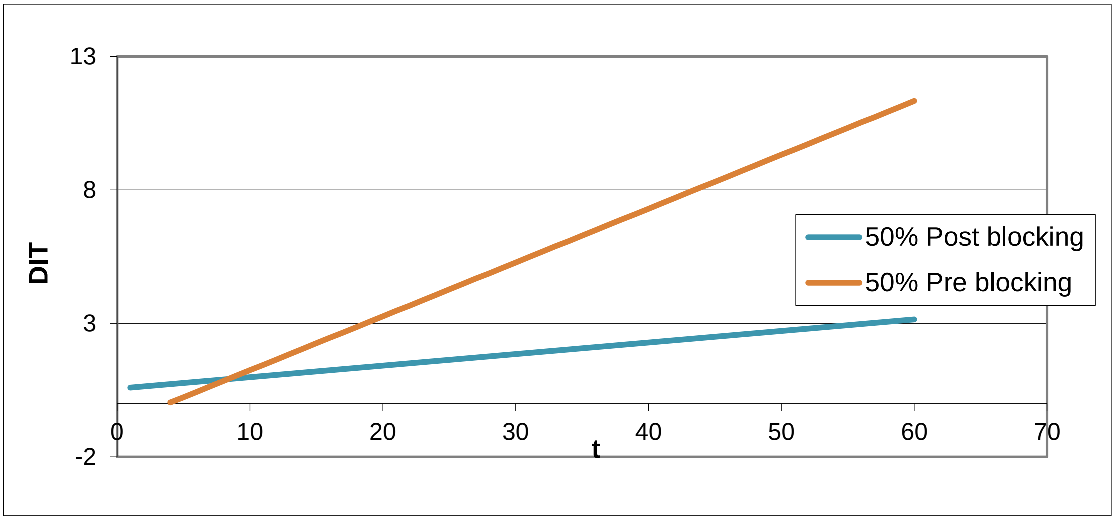


Fig. 4.25: Logistic regression at the 50% probability level for the pre and post blocking period on the experimental catchment on Cronkley Fell.

As discussed in the section 4.4.1 the study sites are natural wet sites with a high water table at the start of monitoring and only a small increase post blocking. The soil therefore has very little capacity to take in extra water falling to the ground and thus water is likely to runoff through the drainage network. This would mean that the flow events recorded are controlled by the characteristics of the rainfall events rather than the antecedent conditions of the ground which is already at or very close to water storage capacity. The data indicates that post blocking the intensity of the rainfall becomes the controlling factor of whether a flow event is likely to occur or not. As the intensity of the rainfall increases the water is increasingly unable to infiltrate into the peat and the water again becomes more likely to runoff through the drainage network.

The controlling factors were not seen to change with scale. The size of both catchments is less than 1km^2 and if the rainfall characteristics are the dominant control on the probability of a flow event occurring, as indicated by the logistic regression, the pattern of the rainfall is unlikely to change in such a small area so once a rainfall event starts in a zero-order catchment it cannot go anywhere else other than the first drain.

4.5. Discussion

The aim of this chapter was to assess whether the blocking of peat drains in the study catchments has had a significant effect on the hydrology and water balance of the area via observations of water table depth and analysis of individual rain storm events. The results showed that although one of the primary aims of drain blocking is to raise the water table closer to the surface this did not happen to any large degree in the demonstration catchments. Water table depth data from the experimental catchment indicates only a slight rise in the water table as the site was naturally wet prior to blocking. Observations of water yield and the catchment hydrograph indicate that blocking has slowed the movement of water through the system, however, there is evidence that during very high intensity rainfall events water will top the blockages and move quickly through the system creating higher than average peaks in the DOC record. This is due to an initial flushing of DOC from the system by the increased water yield. The flow of water over the blockages reflects the small capacity of the peat bog to take in additional water as the peat is naturally close to saturation point. Thus it could be considered that the beneficial effects of blocking i.e. peat rewetting and regeneration will be more visible on areas that are naturally drier.

The failure of the water table to move considerably is however accompanied post blocking by a decrease in water yield. The water yield of the blocked drains has been recorded to decrease by a mean value of 16% on the zero order drains and 12% on the first order drains. With a reduction in water yield of this size a larger decrease in water table depth would be expected indicating that water is being removed from the system in other ways. Water may be being lost from the system by increased evapo-transpiration. However, due to the size of this water yield reduction, evapo-transpiration is unlikely to explain all of it. Rowson (2007) estimates precipitation to be approximately 50% more than evapotranspiration in upland bogs and Petrone et al. (2001) and Essl et al. (2012) found that levels of evapotranspiration do not change significantly upon the rewetting of an upland peat bog. It is therefore likely that the shape and size of the catchment has changed post blocking as water which would have previously exited the catchment via the drains now finds alternative pathways from the system.

The binary logistic regression of the individual rainfall and flow events indicated that blocking had an influence on the probability that a flow event would occur but that this was controlled by the intensity of the rainfall event. This is likely to reflect the overall natural wetness of the ground on to which the rain is falling. The soil has very little capacity to take in extra water falling to the ground thus water is likely to runoff through the drainage network. This would mean that the flow events recorded are controlled by the characteristics of the rainfall events rather than the antecedent conditions of the ground which is already at or very close to water storage capacity both before and after blocking. The data indicates that post blocking the intensity of the rainfall becomes the controlling factor of whether a flow event is likely to occur or not. As the intensity of the rainfall increases the water is increasingly unable to infiltrate into the peat and the water again becomes more likely to runoff through the drainage network.

The event analysis modelling showed no changes in the probability of a flow event occurring with increasing scale. This is likely to be the combined effect of the parameters used to create a best fit model and size of the catchments studied. The parameters used in the logistic regression were the rainfall characteristics and time between events. The catchments studied are both less than 1km^2 and thus these parameters are unlikely to vary in such a small area. However earlier analysis of the drain water yields did show that the size of the water yield reduction post blocking decreases as scale increases. This indicates that water is being lost from the system at some point in the catchment and that further chemical tracing techniques need to be used to trace this missing component of the water balance to establish whether this would affect the efficiency of the drain blocking (Chapter 5).

4.6. Conclusion

This study has used high frequency sampling techniques to investigate any changes in the hydrology of an upland peat bog post blocking. The study found:

1. Blocking had very little impact on the water table of the area with the peat bog being naturally very wet such that when blocking did occur the soil had little capacity to take in additional water.
2. An event analysis approach showed that the dominant control upon runoff events in the upland study catchments is the characteristics of the rainfall events rather than any antecedent condition and that although threshold values changed upon blocking of the drains the dominant control did not.
3. Water yield is seen to decrease by a larger amount post blocking in the zero order drains than in the first order drains indicating that water is bypassing the drain blocks.

5. Chemical tracing of flow pathways and water mixing

5.1 Introduction

Chapter 4 described a detailed hydrological analysis to establish whether any changes in physical hydrology were apparent post drain blocking. The event analysis found that flow events in the upland catchments were predominantly controlled by the characteristics of the rainfall events with the intensity of the rainfall being the primary control post blocking. The water export in the drains was found to decrease significantly post blocking. However this was not accompanied with a significant increase in the water table to account for the additional water present in the catchment indicating that a proportion of the water balance was still unaccounted for. This chapter aims to use chemical tracers to investigate the mixing of different waters in the system and to establish whether the chemistry of the water is seen to change both with scale and upon drain-blocking.

The study uses samples collected during the monitoring period described in chapter 2 to provide an insight into the mixing of waters in the study catchments. Firstly the samples were analysed for pH and conductivity the results of which were used to describe each of the study catchments. Secondly the samples were analysed for major anion and cation content and the results used to conduct a Principal Components Analysis (PCA) in order to describe differences in water chemistry between the sites and after management intervention.

5.2 The use of multivariate techniques

Principal component analysis (PCA) examines multivariate datasets where there are correlations between some or all variables. By seeking patterns in the covariance structure new variables or components are identified representing as much as possible of the variation in the dataset in a smaller number of variables. If there are *m* variables in the dataset, the aim is to find a set of *n* uncorrelated components where *n* is substantially less than *m* but which still explain a large proportion of the variance in the original dataset. The PCA technique is therefore a data reduction or simplification technique because a small number of components explain a larger proportion of the variance in the dataset than could be explained by any combination of the same number of original variables. Once identified the components can then be transformed into the terms of the original variable set and used for further analysis, as the output for each of the *n* components is a coefficient or loading for each of the variables in the original dataset, so each observation can be assigned a score for each retained component by multiplying the observed value for each variable by the loading for that variable.

5.2.1 Details of the Principal Component Analysis Method

Principal component analysis is a multivariate exploratory data analysis technique for use with datasets where the variables are “on an equal footing” (Chatfield and Collins, 1980): that is, there are generally not separate explanatory and response variables for each observation. The technique involves the transformation of a set of variables some or all of which may be correlated to a new set of uncorrelated components consisting of linear combinations of the original variables. There are three main motivations for this approach.

Firstly the identification of the components may help to identify any underlying linear structure, trends or dimensions in a multivariate dataset. For example, Haag and Westrich (2002) identified underlying controls on river water composition such as biological processes and discharge from an original variable set consisting of numerous directly-measured water parameters such as conductivity, pH and temperature. The identification of explanatory trends in this way is accomplished primarily by observation of the grouping of variables into components, in the hope that variables that can be identified as being related to a common cause will be found to be strongly related to a common component. The fact that principal components are uncorrelated helps ensure that each one is measuring a different dimension or trend in the data (Manly, 1986).

Chatfield and Collins (1980) argued that the use of PCA to identify linear structures in data achieves little that could not be done by a direct analysis of the correlations between the variables, but equally the analysis of the components in this way can be taken further than implied by Chatfield and Collins (1980). For example, one real-world source of trends or dimensions in the underlying data is where samples are taken representing mixtures formed from different combinations of end-members. In this case PCA can identify the trends in such a way as to point toward and even identify the mixing end-members as demonstrated in an idealised example by Davies (2005) for a situation where the measured variables would be too numerous and too extensively correlated for such trends to be readily observed from the correlation matrix.

The second reason for using PCA is the reduction in the dimensionality of the data that can generally be achieved. Since each component may represent the variance for several variables and since the components are orthogonally rotated such that they are in decreasing order of the amount of variance explained, the first few components may represent most of the variance from the original data set, meaning that a larger proportion of the variance can be described by fewer variables than was possible with the original data set. Since the components are also orthogonal or uncorrelated, this is a useful technique prior to, for instance, multiple regression which can then be conducted on the components rather than the original variable.

The third reason is as a variable reduction technique. Since components are ranked in order of the amount of variance in the original dataset that is explained, variables that do not correlate strongly at any component or only correlate strongly to components which explain little of the overall variance can be seen to contribute little information to the overall dataset. Once again this can be a useful technique prior to other analysis such as multiple linear regression, this time directly on the remaining original variables once those shown by the PCA to be irrelevant have been discarded.

The general technique of PCA was first suggested by Pearson (1901) and one of the first practical methods for computing the technique was proposed by Hotelling (1933). Principal components are calculated from the covariance matrix of the variables, generally after the variables are standardised to zero mean and unit variance - this is the equivalent to saying that the components are calculated from the correlation matrix. If the variables are not standardised (principal components are calculated from the covariance matrix directly) then the variables are required to all be on the same scale to ensure equal weight in the analysis.

The eigenvalues of the correlation matrix **c** are equivalent to the variance of the principal components and the coefficients of the principal components in terms of the standardised variable are given by the eigenvectors of **c**. These are selected and allocated to the principal components (PCs) in an iterative process by finding at each stage the combination of the coefficients such that the variance of the PC is maximised and (for all components except the first) such that the eigenvector is orthogonal to each of those already selected. This process is explained fully in Chatfield and Collins (1980). One key point to note is that there is an arbitrary choice of sign in the choice of the eigenvectors (due to the presence of square root terms in the matrix manipulation) and so the overall sign of each PC is also arbitrary. Additionally if there are linearly dependent variable in the dataset (correlation = 1) then some eigenvalues will be zero; the number of linear constraints that can be found on the variables is equivalent to the number of zero eigenvalues.

Since the eigenvalues of the correlation matrix add to the sum of the diagonal terms (each of which is 1 in a correlation matrix) so too do the eigenvalues of the PCs, i.e. the total of the eigenvalues of the PCs is equivalent to the number of variables when analysis is conducted on the correlation matrix. This gives rise to a common algorithm for determining the number of PCs to retain in the analysis when the analysis is based on the correlation matrix: all PCs with an eigenvalue > 1 plus the first PC with eigenvalue <1. This is appropriate because PCs with an eigenvalue >1 are those which explain more variance than any one of the original variables could – this study used this rule.

5.2.2 PCA as a mixing analysis technique

Principal component analysis has been described by Davies (2005) as being of use in "*identifying underlying structures in the dataset connecting causes of variability across several variables, allowing reduction of the dataset into a smaller number of components and interpreting these causes in terms of real world influences*". It is the potential for PCA to be a variable reduction technique, representing combinations of the input variables as a smaller number of underlying components or factors. This is of relevance to mixing analyses and hence to studies of catchment behaviour because conservatively-mixing waters that can be represented in terms of end members introduce precisely the kinds of patterns into the data collected from samples that PCA has been shown to be of use in identifying (e.g. Davies, 2005). Samples formed from various combinations of several end members, provided that those end members mix conservatively, will have compositions that can be described in terms of linear compositions of those end members. This is known as end-member mixing analysis (EMMA) (Hooper, 2001, 2003). Principle component analysis can provide a method for achieving a similar result when the compositions of the end members are not known (Davis, 2005).

The basic method is to plot PC scores for one component against another and to examine the distribution of those scores; often these will form a clearly-identifiable pattern or shape with end members at vertices. The principle components themselves do not identify end members; that is, the end members will not necessarily lie on the axes of the PC plot. Rather each principal component is assumed to represent a process or pattern in the mixing of the end members and plotting scores of the principal components against one another will then reveal the end member data points.

5.2.3 Previous studies

A wide range of previous studies have shown the use of PCA for identifying trends in multivariate datasets collected from water samples across a catchment over a range of times and locations. The majority of these have been concerned chiefly with interpreting the results in terms of underlying mechanisms or factors, whilst a smaller number have conducted more detailed analysis of the trends between the identified components, rather than the loadings on the components, in order to make inferences about mixing sources or other catchment behaviour.

Haag and Westrich (2002) studied the River Neckar in Germany, collecting samples from each of six sites along the main river over a five-year period analysing these for Chlorophyll-a, BOD, Conductivity, pH, water temperature, ammonium, nitrite, nitrate, phosphate and dissolved oxygen. After PCA on the entire dataset four components were retained. The loading on these components were such that Haag and Westrich (2002) were able to interpret each component as representing a different set of influences on the water quality according to which variables had high loadings on each component and knowledge of what natural processes influence each variable.

Petersen et al. (2001) analysed samples collected fortnightly over a five year period from 14 sites on the River Elbe in Germany. The samples were once again analysed primarily for nutrients rather than inorganic solutes and as with Haag and Westrich (2002) the study was therefore concerned chiefly with identifying underlying organic and biological controls on the water quality rather than geological or geographical controls such as rock type. Petersen et al. (2001) introduced a LOWESS smoothing method for the elimination of external forcing caused by discharge and temperature; the method was later used by Haag and Westrich (2002). Once again Petersen et al. (2001), whilst concerned primarily with organic influences demonstrated the utility of PCA as a technique for identifying underlying influences from a diverse set of water quality variables. Petersen et al. (2001) also applied the bootstrap method (eg Efron, 1986) in the estimation of the component loadings enabling the generation of “pseudo” confidence intervals for the variable loading estimates.

The studies described above illustrate the use of PCA for identifying underlying factors behind the observed composition of river waters. However they pertain primarily to the results of processes operating within the river itself. Christophersen and Hooper (1992) discuss the use of PCA specifically for analysis of mixing of source waters and compare the technique to the more classical end-member mixing analysis (EMMA). The authors state that EMMA is appropriate if source waters are available that are indeed extreme enough to be considered *a priori* as “end members”- for instance soil water and precipitation- and if their combination is known, in which case a least-squares method is used to identify the combination of source waters present in each stream sample. Mathematically the technique is similar in concept to solving simultaneous equations. This approach is known as a “forward analysis” (Christopher and Hooper, 1992): PCA provides the reverse approach. The use of PCA attempts to identify from the samples the number and composition of the source water end members. The components do not necessarily represent end members themselves but rather underlying patterns in the data, which can be combined to represent end members. Christopher and Hooper (1992) give the example of a component loading strongly on hydrogen ions, sulphate and nitrate representing an acid component; this does not means that a given dataset will necessarily contain samples with large scores only on this component but rather that there may be samples scoring positively on this component and negatively on another component. That is, the end members do not necessarily lie on the axes of the space defined by the components, but when the scores of various components are plotted against one another the end members can be observed as circumscribing the data.

Christopher and Hooper (1992) argue that this PCA approach cannot unambiguously identify the source water compositions and is therefore not always appropriate in stream sampling, because a given dataset does not necessarily include samples of each end members. The PCA analysis cannot identify end members that lie outside the space sampled. However the authors accept that PCA is nonetheless useful in determining the number of end members (source waters) and in suggesting potential compositions. These proposed end member compositions can then be analysed by a forward EMMA technique to determine how well they can predict the observed stream compositions and therefore to judge how appropriate the results of the PCA are.

Worrall et al. (2003) demonstrated the use of PCA for mixing analysis and the identification of end members in upland areas, applying the technique to samples collected from a range of sites and sub-catchments across the 11.4km^2 Trout Beck Catchment, North Pennines. The study identified five key principal components, representing respectively overall concentration; Fe, Al and colour; K; N and Na; K and Cl. Analysis in this study was largely in terms of the trends in samples indicated by the principal components, used to trace the source and evolution of sample waters, rather than in terms of identifying underlying processes or factors as in some other studies such as Haag and Westrich (2002) and Petersen et al .(2001). Having run a single PCA on the bulk data of all samples and solutes collected for the study, Worrall et al. (2003b) conducted an extensive analysis of the results of the PCA to assess not only mixing of the waters, but also the evolution of the waters from the source end members. This was achieved by comparing samples along potential flow paths from precipitation and ground water, through soil water to streamflow. For example, the study assessed the evolution in chemistry of soil waters over time and compared this to the chemistry of the precipitation, leading to the conclusion that soil water was well buffered against changes in precipitation chemistry (Worrall et al., 2003b).

Worrall et al. (2006) analysed long-term water quality from the same upland peat catchment in the north Pennines in order to understand long term changes in hydrological flow paths and how they relate to recovery from severe drought and control the release of DOC. The study examined single tracers and used multivariate statistics to examine changing sources and run off pathways. Principal component analysis was performed on samples of rainwater, soil water and stream water analysed for pH, conductivity, calcium, magnesium, potassium, sodium, iron, aluminium, chloride, sulphate and total N. The study found that soil and stream water samples from the study catchment can be described by a three end-member system consisting of summer rainfall, winter rainfall and shallow soil water. Also the study found that changes in the proportion of end-members in the stream waters during the drought period indicate increased residence times in the shallow peat horizons and a lessened influence of rainwater on the deep soil waters.

This study aims to use individual chemical tracers and PCA techniques to investigate the mixing of different waters in the system and to establish whether the chemistry of the water is seen to change both with scale and upon drain-blocking or indeed whether this indicates changes in flowpaths through the study catchments. The study uses both conservative and non-conservative tracers. Conservative tracers will remain constant during their movement through the system whereas non-conservative tracers (such as compounds undergoing a mutual chemical reaction) will decay with time meaning that their reliability is limited over longer periods (Davies, 1991). This study uses a large range of conservative and non-conservative tracers so that the impact of any degradation of the non-conservative tracers will be reduced. Also the movement of water through the studied catchments is relatively fast meaning that the chance for degradation of the tracers to occur is limited.

5.3 Methodology

5.3.1 Sampling and analysis protocol

During the sampling campaigns described in chapter 2 to monitor DOC export from the drain sites at Cronkley Fell regular site visits were made to collect the automatic samples. On these visits manual grab samples were also collected. On return to the laboratory these samples were frozen prior to anion and cation analysis. All samples were also analysed in laboratory for pH and conductivity using handheld electrode methods (error: ±0.01 pH and ±1% conductivity) and for DOC concentration (error: ±2mg/l DOC), the method for which is described in chapter 2.

The concentrations of Al, Ca, Fe, K, Mg and Na was analysed using ICP-OES (Inductively Coupled Plasma- Optical Emission Spectroscopy) in selected water samples. Analysis was conducted on filtered samples using a Perkin Elmer Optima 3300 RL ICP-OES machine and ICP Winlab was used for a machine control and data processing. Mixed standards for analysis were produced using Romil ICP standards and a serial dilution technique. Standards (including blanks) were run prior to the analysis and the 50 and 25mg l^{-1} Ca standards were re-analysed as samples approximately every 25 samples as a manual check for drift; additionally all standards were re-analysed at the end of each run. Two wavelengths were collected for each element except K, and all calibration curves used for data processing had R^2 values > 0.99 for all elements. Instrument drift was corrected during the data post-processing using the internal standard method. Yttrium was selected for the internal standard as it was not found at detectable levels in any samples. All standards and samples were “spiked” with 1 mg l^{-1} Y. Optical sensor output counts for each element are converted into mg l^{-1} concentrations by comparing counts for Y between samples and standards so the Y spike must be accurately metered. Pipettes used were calibrated using a 5-place balance. Samples were acidified using 10 mg l^{-1} HNO_3; this was found necessary to prevent flocculation of the samples on addition of the Y spike and subsequent clogging of the ICP sampling mechanism. Analysis was conducted on unfiltered samples which were stored frozen in sealed containers prior to analysis; samples were analysed immediately following the addition of the HNO_3 and the Y spike.

Ion chromatography was used to analyse the water samples for: fluoride (F), bromide (Br), chloride (Cl), nitrate (NO_3), phosphate (PO) and sulphate (SO_4). Ion chromatography is a form of liquid chromatography which measures concentrations of ionic species by separating them based on their interaction with a resin. Ionic species separate differently depending on species type and size. Samples are passed through a pressurized chromatographic column where ions are absorbed by column constituents. An ion extraction liquid runs through the column and the absorbed ions begin separating from the column. The retention time of different species determines the ionic concentrations in the sample. Selected filtered samples from a range of flow conditions were subjected to IC analysis.

The instantaneous flow within the drains at the time the sample was taken was also monitored as described in chapter 2.

5.3.2 Statistical Analysis

The data collected underwent a process of PCA in which the aim was to identify the nature of water mixing within the catchments. All chemical and flow data was analysed to identify the principal components which describe the water chemistry of the catchments. A total of 1627 water samples were analysed. Each of these samples was analysed for 15 parameters; pH, Conductivity, DOC, Al, Ca, Fe, K, Mg, Na, F, Br, Cl, NO_3, SO_4 and peak instantaneous discharge. These parameters however have different units which makes their comparison in PCA unreliable. As such all data were transformed to standard normal distribution using a Z-transform prior to analysis. Where the Z-transform is:

$$z = \frac{x - \mu}{\sigma}$$

Where: x is a raw score to be standardized; μ is the mean of the population; and σ is the standard deviation of the population. The quantity z represents the distance between the raw score and the population mean in units of the standard deviation: z is negative when the raw score is below the mean and positive when above.

The process of PCA was performed on all the data from the control and experimental catchments at all scales. Flow was initially used as a component in this analysis however it quickly became apparent that the inclusion of flow greatly affected the fit of the model and as such it was excluded from the subsequent PCAs. The number of components to retain was determined by including all those with an eigenvalue > 1 and the first component with an eigenvalue < 1. The scree test was also applied for visual selection of the components. Once the PC values had been calculated plots of PC1 against PC2 were created for the control catchment and for the experimental catchment both pre and post blocking to enable the identification of any end members and describe the nature of any water mixing.

Following PCA certain components were subjected to a process of analysis of variance (ANOVA) using the method described in chapter 2. ANOVA was performed on the PC1 values from the experimental catchment in order to establish whether these values were seen to vary significantly post blocking. Scale and blocking status were considered as factors in the ANOVA. Both these factors have two levels zero and first order for scale and blocked and unblocked for the blocking status. The ANOVA also considered the following as covariates: DOC, pH and conductivity.

5.4 Results

5.4.1 pH and Conductivity

The construction of comparison plots for pH and conductivity for both the experimental and control catchment indicate a change in water chemistry from zero to first order streams. The effects of dilution discussed in chapter 2 and 4 are visible again with both the control catchment (Fig. 5.1) and the experimental catchment (Fig. 5.2 and 5.3) showing an increase in pH as water moves from the zero order to first order streams.

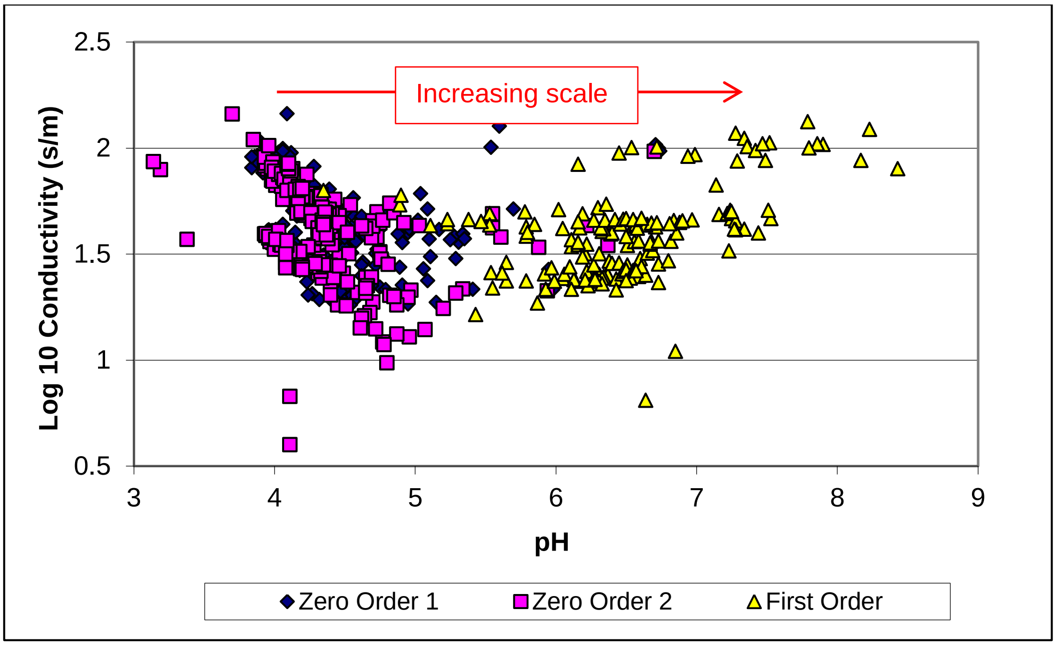


Fig. 5.1 Comparison plot for Control Catchment on Cronkley Fell

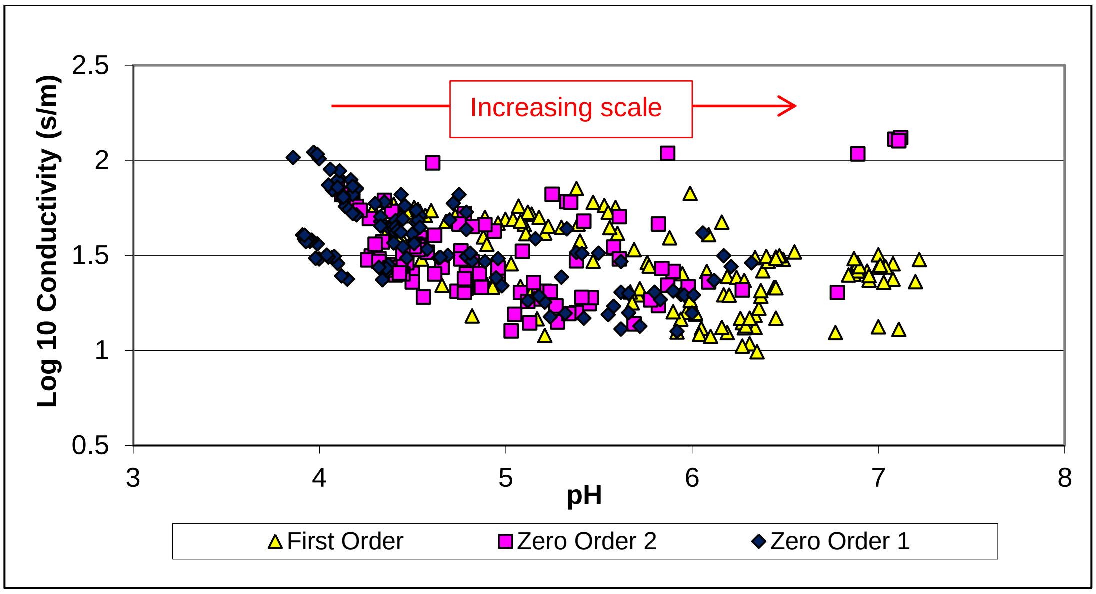


Fig. 5.2: Comparison plot for pre-blocking period of the experimental catchment on Cronkley Fell

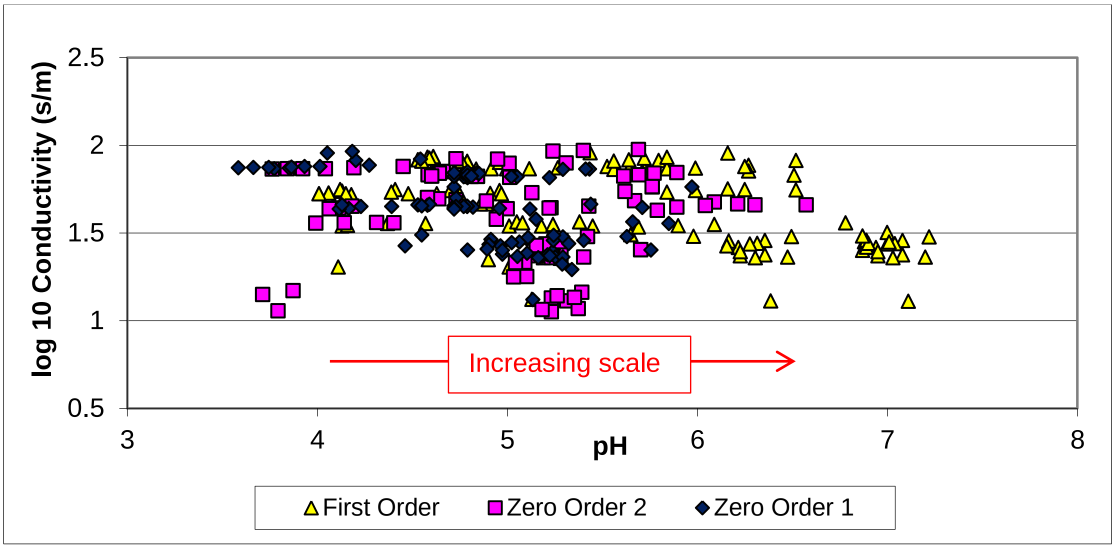


Fig. 5.3: Comparison plot for post-blocking period of the experimental catchment on Cronkley Fell.

5.4.2 Solute concentration results

The distributions of the concentrations of each metal included in the analysis are shown in Figure 5.4. Similarly Figure 5.5 presents the results for the anion concentrations. Analysis of water samples for anions found negligible concentrations of fluoride, bromide and phosphate as such these figures are not included.

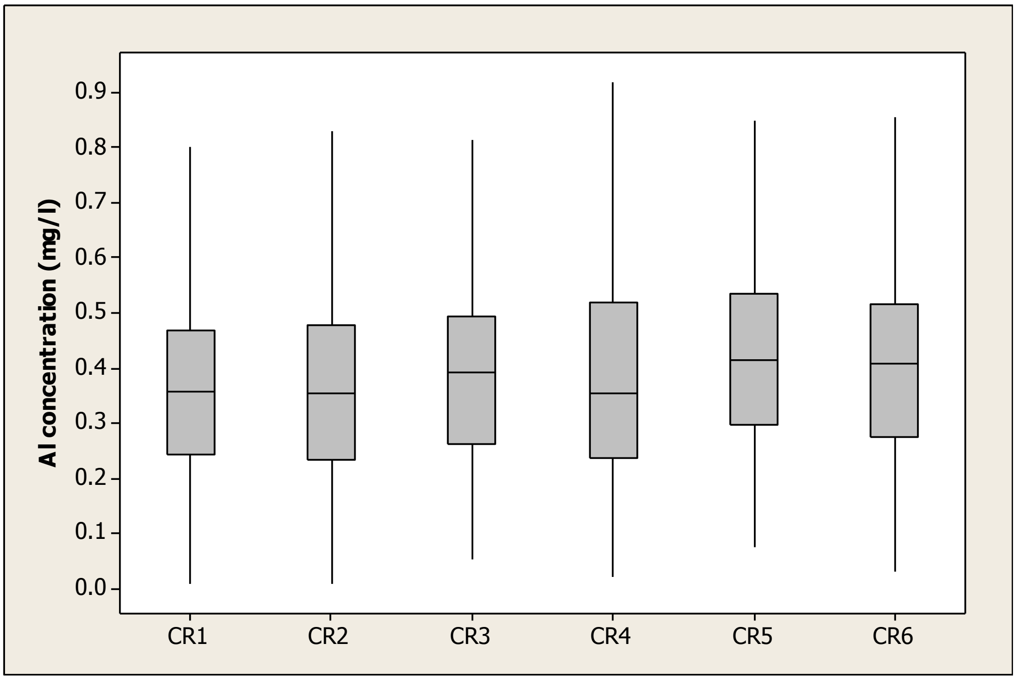


Fig. 5.4a: Box plot of Al concentration for Cronkley Fell

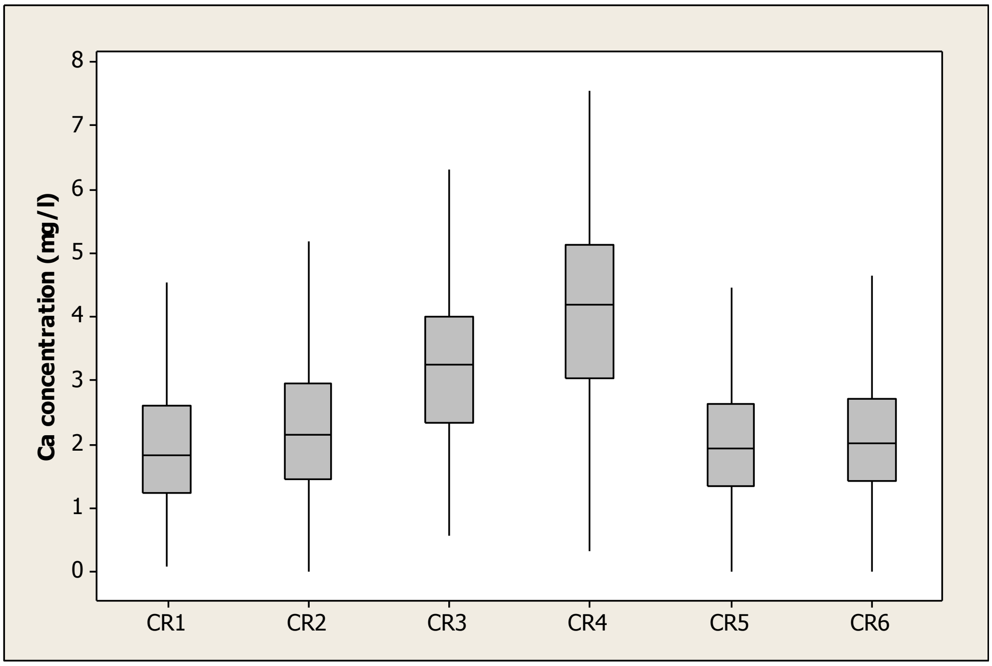


Fig. 5.4b: Box plot of Ca concentration for Cronkley Fell

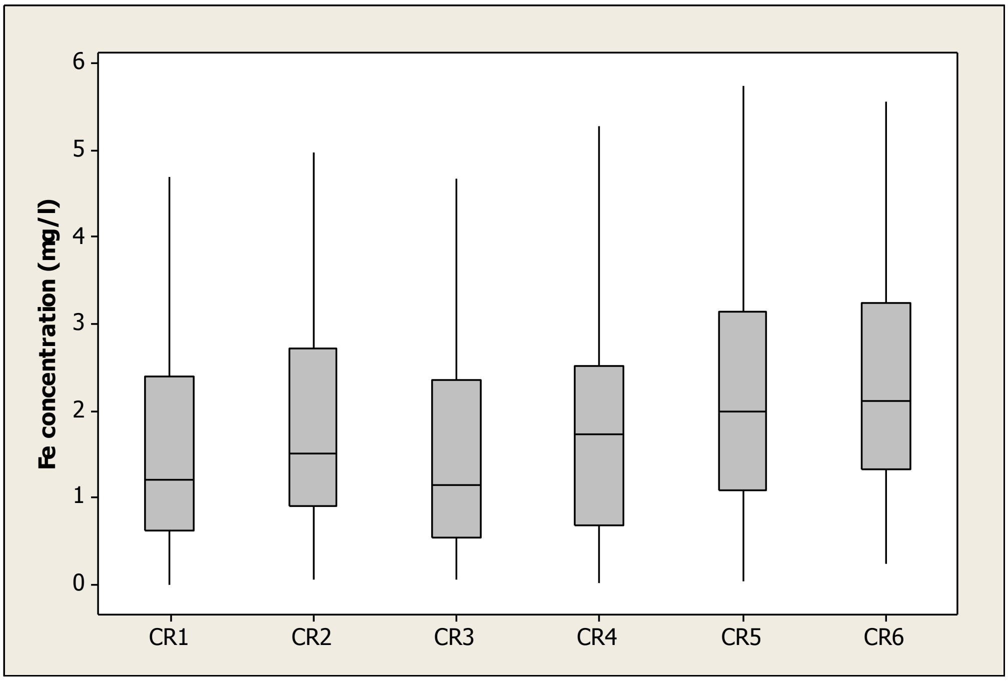


Fig. 5.4c: Box plot of Fe concentration for Cronkley Fell

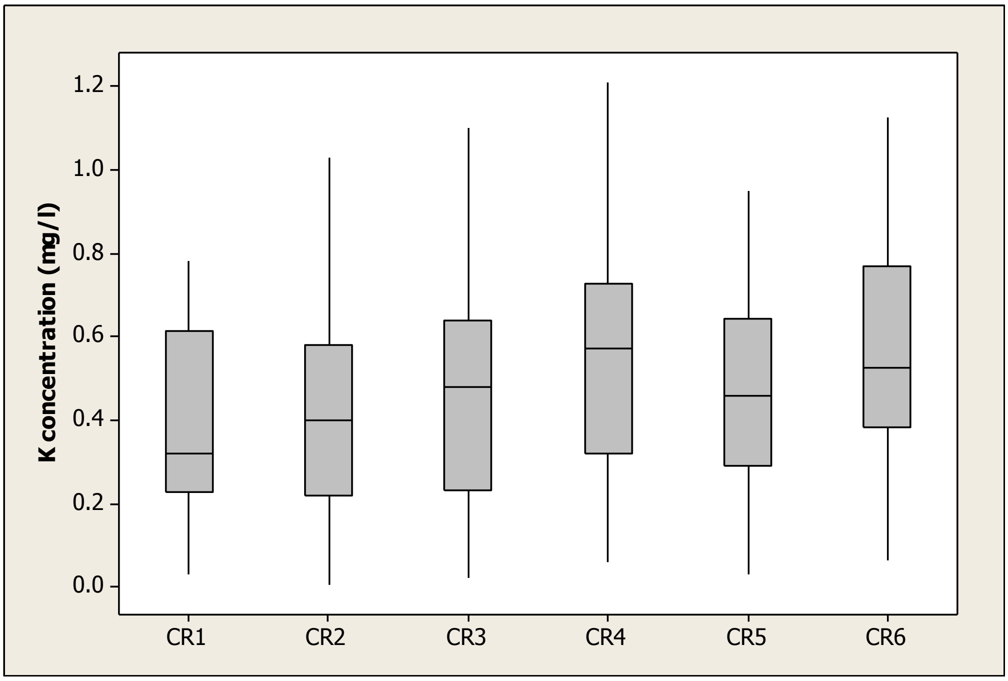


Fig. 5.4d: Box plot of K concentration for Cronkley Fell

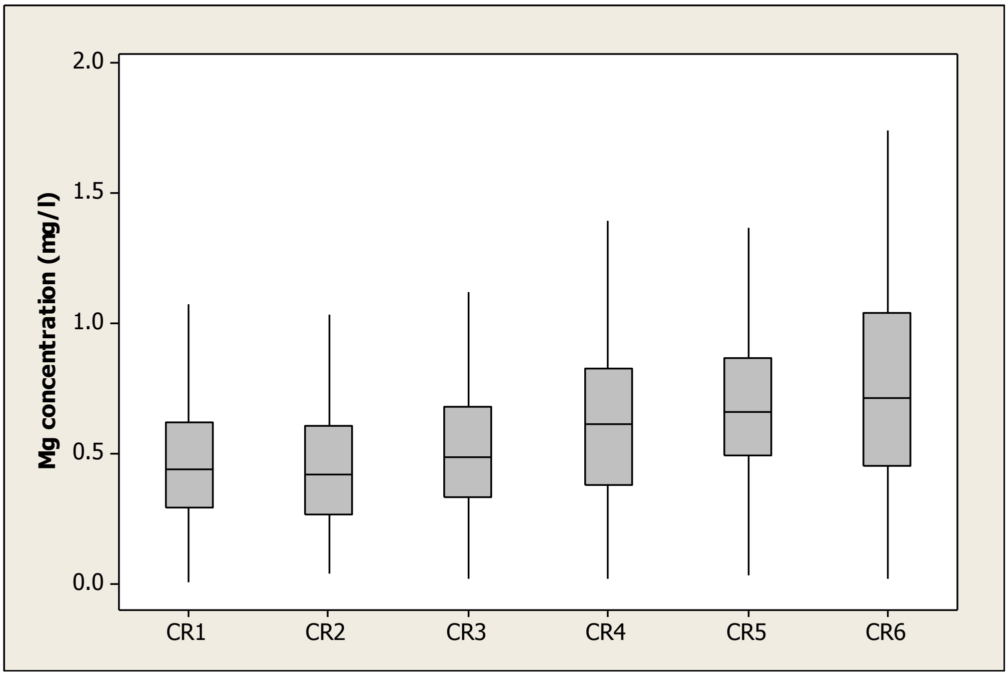


Fig. 5.4e: Box plot of Mg concentration for Cronkley Fell

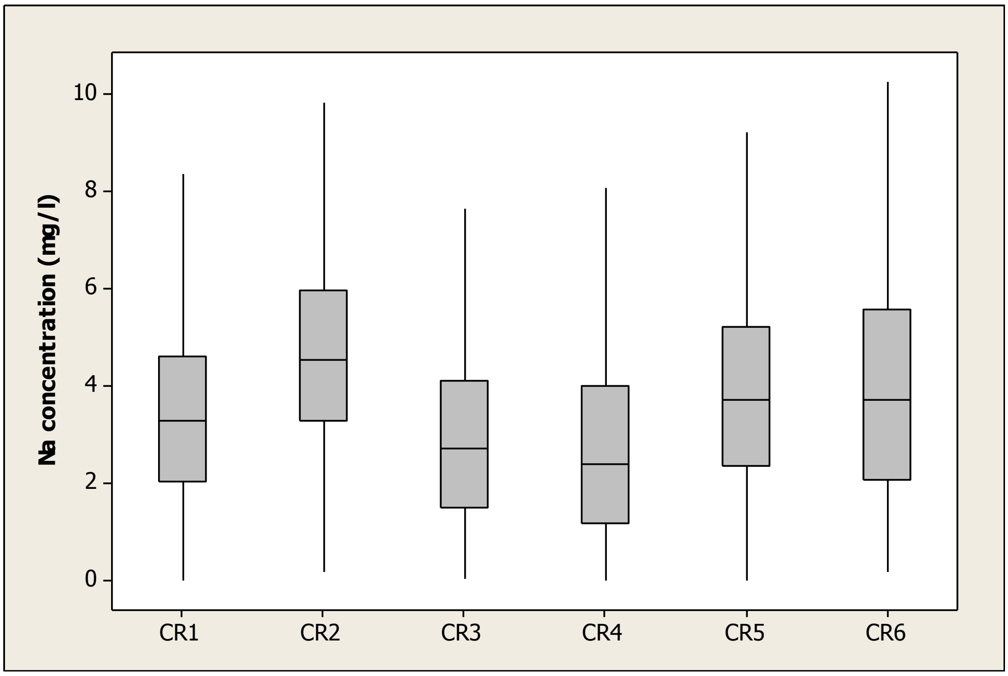


Fig. 5.4f: Box plot of Na concentration for Cronkley Fell

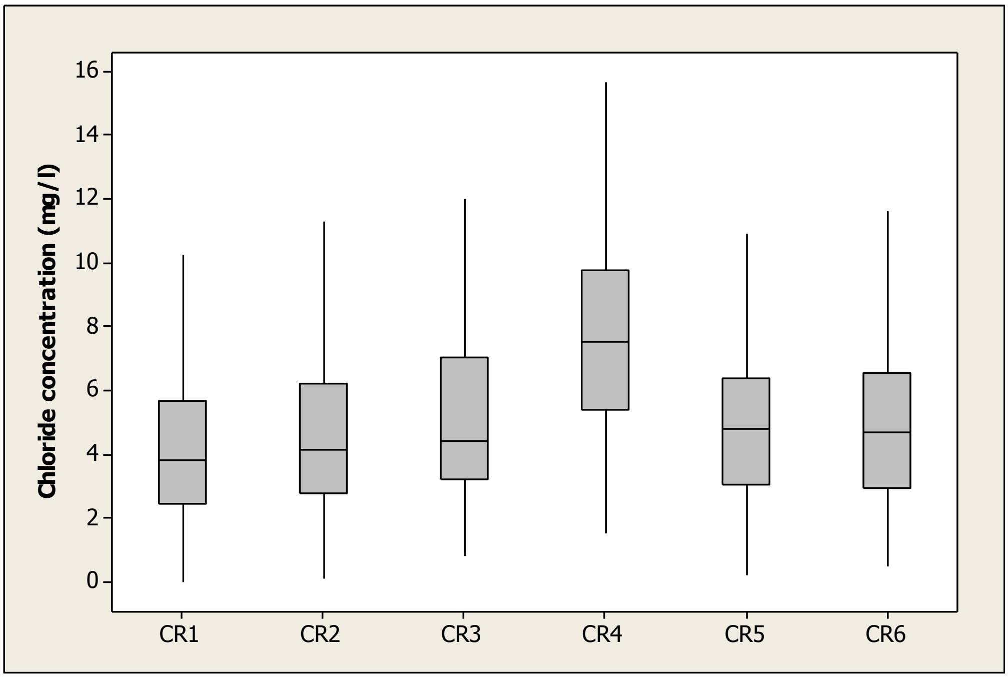


Fig. 5.5a: Box plot of Chloride concentration for Cronkley Fell

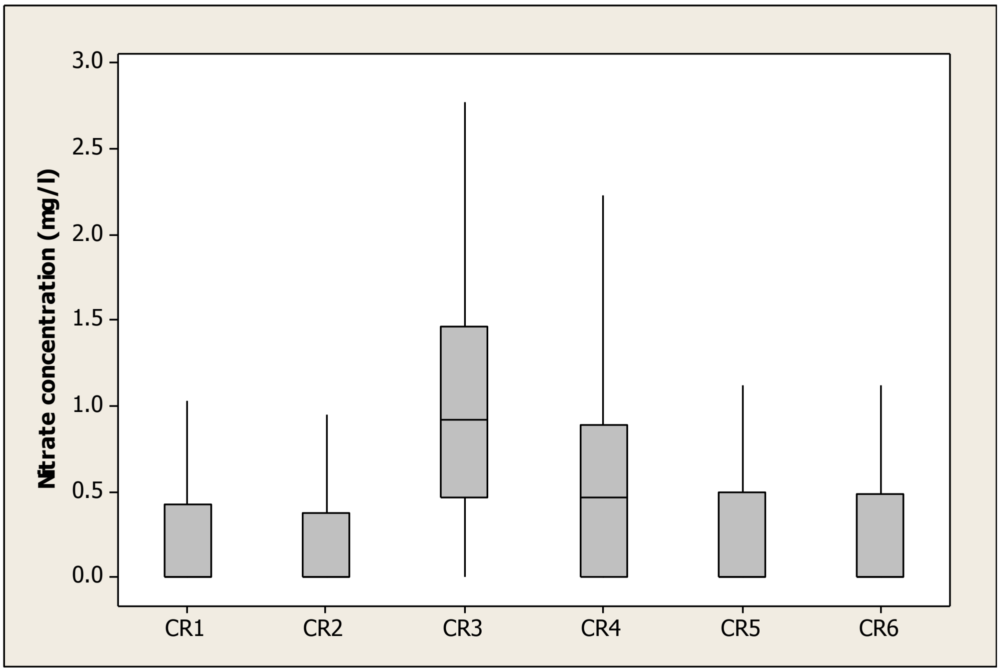


Fig. 5.5b: Box plot of Nitrate concentration for Cronkley Fell

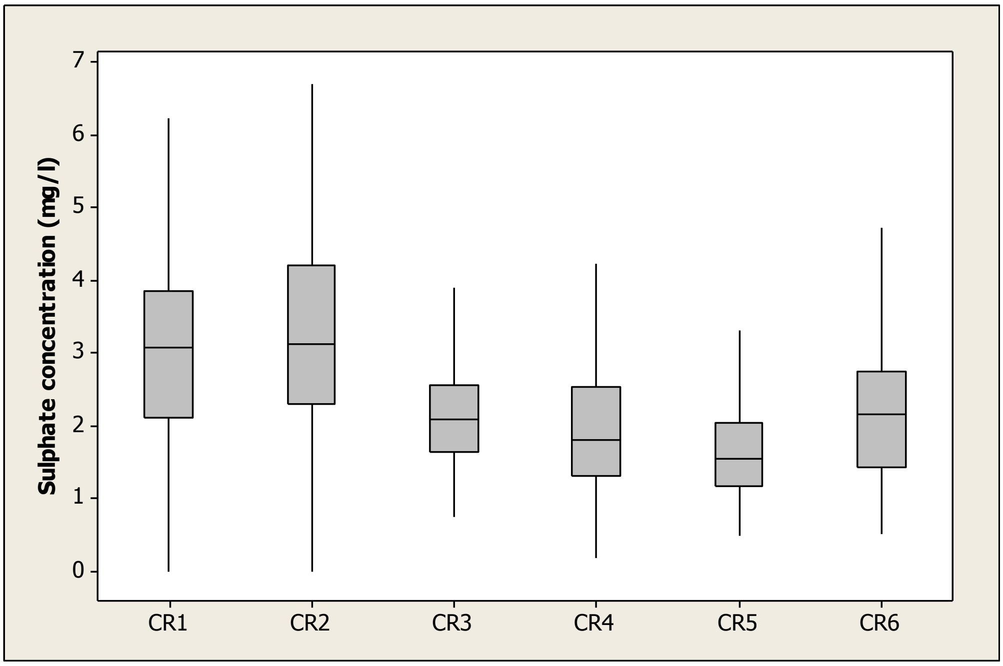


Fig. 5.5c: Box plot of Sulphate concentration for Cronkley Fell

5.4.3 PCA results

The comparison of the eigenvalues suggested the retention of seven components (Table 5.1) however it is clear from the scree plot (Fig 5.6) that of these seven components the first two components can be used to determine the difference between the majority of the water samples.

Variable	**1**	**2**	**3**	**4**	**5**	**6**	**7**
pH	0.504	0.001	0.110	0.005	0.030	0.146	-0.005
Conductivity	-0.053	0.168	-0.475	-0.003	0.274	-0.168	0.351
DOC	-0.504	0.031	0.00	-0.189	0.049	0.072	-0.169
Aluminium	0.024	-0.267	-0.446	0.371	0.123	0.235	0.262
Calcium	0.380	0.181	-0.144	-0.238	-0.170	-0.050	-0.230
Iron	-0.019	-0.447	-0.158	-0.086	-0.512	-0.90	0.002
Potassium	0.170	0.063	-0.394	-0.007	0.088	-0.610	-0.182
Magnesium	0.048	-0.261	-0.437	0.044	0.181	0.347	-0.361
Sodium	-0.237	-0.244	-0.229	-0.297	-0.369	0.018	-0.205
Fluoride	0.128	-0.197	0.126	-0.177	0.403	-0.100	-0.482
Chloride	0.249	0.398	-0.255	-0.202	-0.208	0.139	-0.078
Bromide	-0.017	-0.284	0.036	-0.370	0.476	0.015	0.046
Nitrate	0.333	-0.190	0.047	-0.251	-0.023	0.412	0.232
Phosphate	0.043	-0.164	0.005	-0.538	0.021	-0.242	0.477
Sulphate	-0.254	0.440	-0.188	-0.332	0.080	0.359	-0.005
Eigenvalue	2.113	1.252	1.214	1.149	1.123	1.031	0.988
Proportion of variance	0.141	0.084	0.081	0.077	0.075	0.069	0.066
Cumulative of variance	0.141	0.224	0.305	0.382	0.457	0.526	0.592

Table 5.1: Results of retained components of PCA on all samples

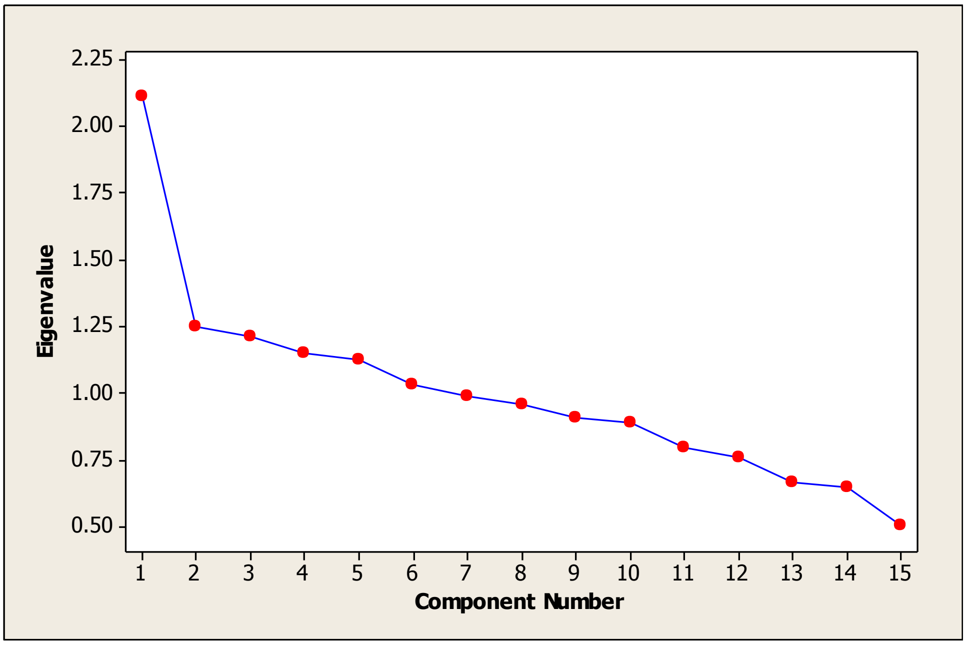


Fig.5.6: Scree plot of the eigenvalues for the PCA analysis

Component 1 has strong positive loadings on pH (0.504) and strong negative loadings on DOC (-0.504) (Fig. 5.7). The first component is often found in PCA to represent some measure of overall concentration or size (as appropriate to the data) (Worrall et al., 2003b), however, this would not be the case for Z-transformed data as used here. The large eigenvalue of component 1 and the high proportion of variance that it explains suggest that by far the greatest difference between samples is in terms of the overall DOC concentration and pH. Component 2 distinguishes primarily between sulphate and chloride (strong positive loadings; 0.440 and 0.398 respectively) and iron and sodium (strong negative loadings; -0.447 and -0.244 respectively). This component however has a much smaller eigenvalue and explains a notably lower proportion of the variance again suggesting that the chemical variation in the water samples collected can be explained by changes in pH and DOC concentration.

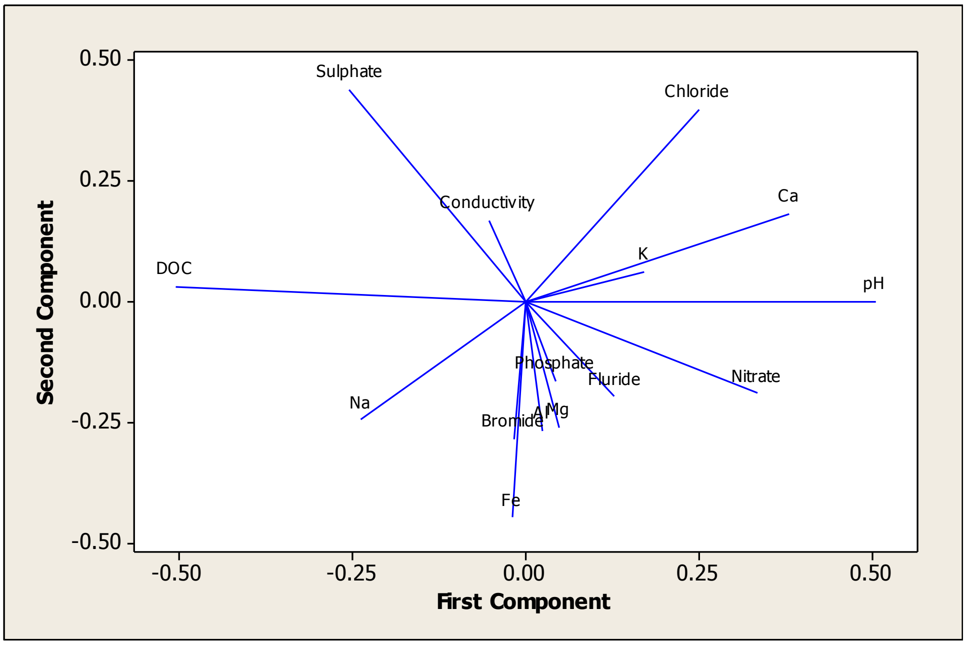


Fig. 5.7: Loading plot of PC1/PC2

When the PC1 scores are plotted against PC2 scores (Fig. 5.8 and Fig. 5.9) a clear trend is visible when moving from the zero to first order drains in both the control and experimental catchments. For both catchments as the drain scale increases the PC1 values are seen to shift towards the positive end of the axis. No notable change in PC2 scores is recorded as scale increases. This distribution in the data not only agrees with what was demonstrated in the pH and conductivity plots in Figure 5.1, 5.2 and 5.3 but also suggests that the water in the catchment can be described by a relatively simple mixing model where water chemistry is seen to change with scale due to variations in pH and DOC concentration.

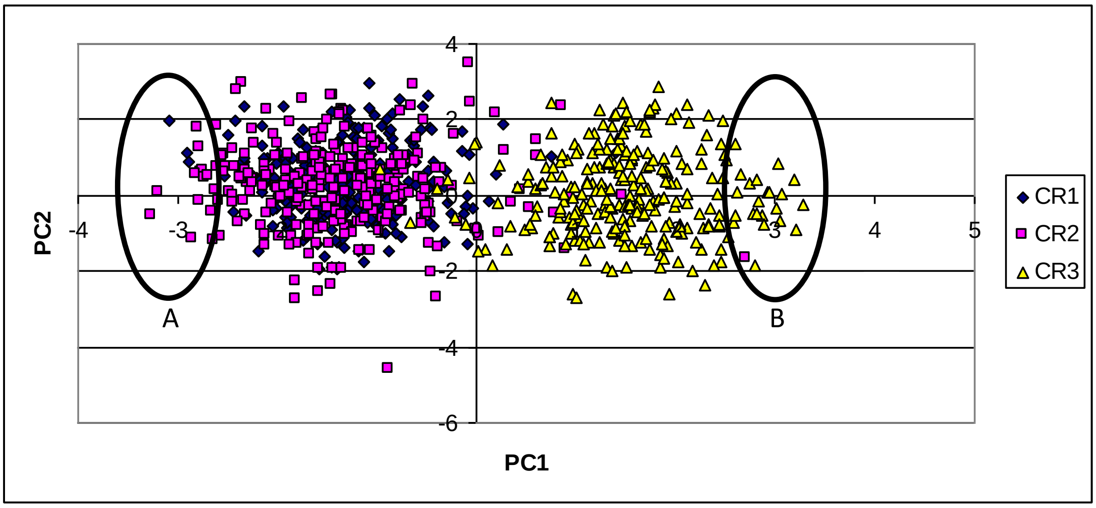


Fig. 5.8: Score plot of PC1/PC2 for all samples taken on the control catchment on Cronkley Fell. A and B represent end member regions.

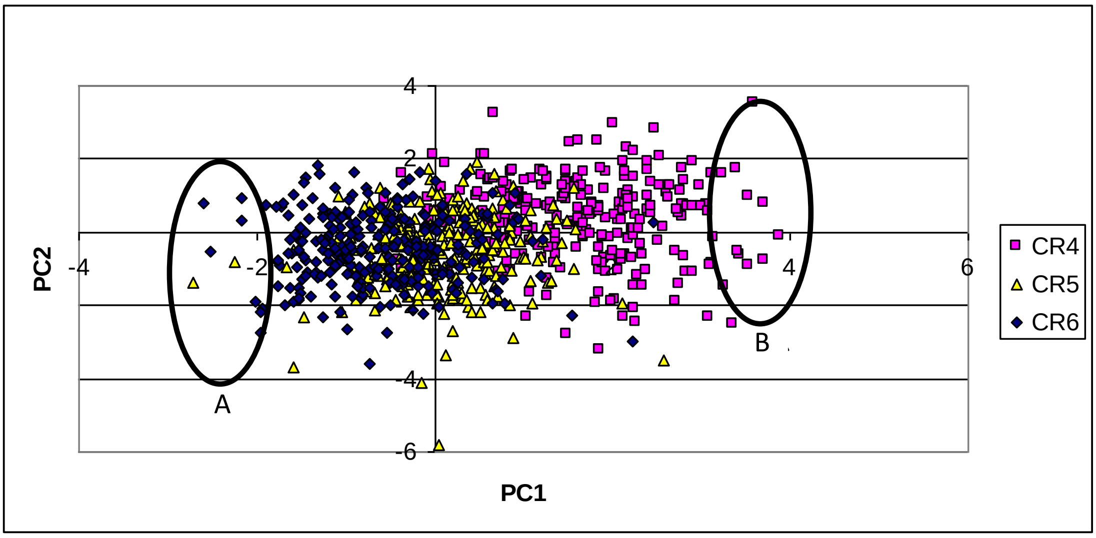


Fig. 5.9: Score plot of PC1/PC2 for all samples taken on the experimental catchment on Cronkley Fell. A and B represent end member regions.

Chapter 2 demonstrated that DOC concentration is seen to decrease with increasing scale due to the greater effect of dilution. This dilution effect would also explain the increase in pH seen upscale in Figures 5.1 and 5.2. The relatively simple mixing model that the results indicate, suggests that water in the catchment can be classified along a general mixing trend rather than by a series of specific end members. Despite this, two general end member regions can be defined (labelled A and B in Fig 5.8 and 5.9). End member A describes a high DOC concentration, low pH water which is predominantly found in the zero order drains of the catchments. The water at this scale has not experienced the effects of dilution or processes that may lead to DOC loss such as degradation. End member B describes a low DOC concentration, high pH water which is chiefly found in first order drains of the catchment. The water that has reached this point of the catchment has experienced a greater level of dilution than the water in the zero order drains and will have undergone the DOC loss processes discussed in chapter 3. The majority of the water samples collected are seen to lie on a mixing trend in between these two end member regions.

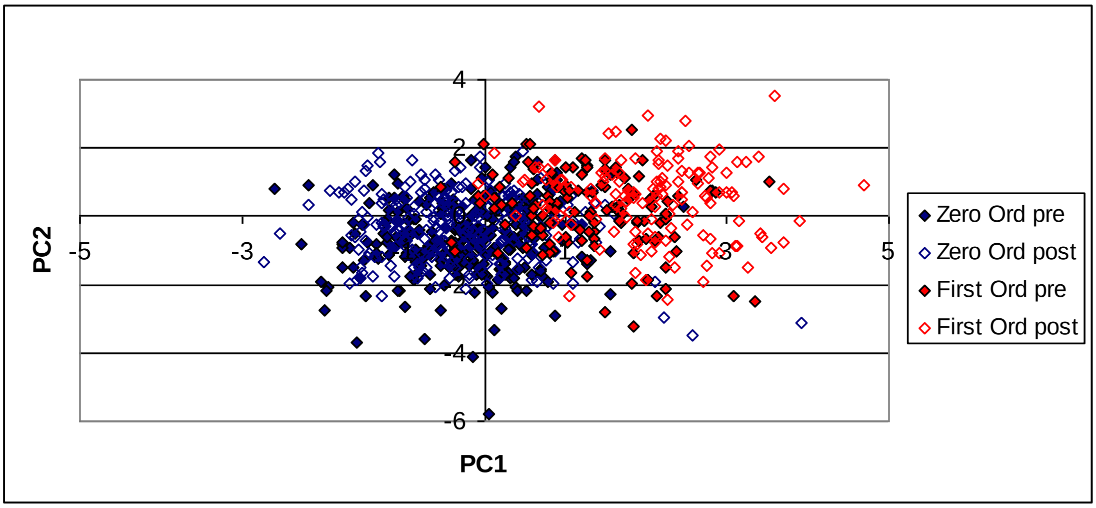


Fig. 5.10: Score plot of PC1/PC2 for the zero and first order drains in the pre and post blocking period for the experimental catchment on Cronkley Fell.

Factor	**P**	**Proportion of variance (%) without covariates**	**Proportion of variance (%) with covariates**
Scale	<0.001	45.2	22.3
DOC	<0.001		12.4
pH	<0.001		9.1
Month	>0.5		
Blocking	>0.5		
Conductivity	>0.5		
Error		54.8	56.2

Table 5.2: ANOVA of PC1 scores giving the probability of the factor/interaction and the proportion of the variance explained by the factor.

The PCA has shown that the water chemistry changes with scale. However it is also important to determine whether the effect of blocking has had any effect on the mixing trend demonstrated above. The PCA scores for the experimental catchment were thus plotted in terms of pre and post blocking (Fig. 5.10). ANOVA was then performed on the PC1 scores to establish whether any significant changes in its value could be recognised post-blocking (Table 5.2). It was found that blocking did not have a significant effect on the value of PC1 indicating that the process of blocking does not appear to have had an effect on the mixing trend in terms of pH and DOC concentration. The ANOVA did suggest that scale and the covariates DOC concentration and pH had a significant effect on PC1 scores concurring with what was inferred from Figures 5.8 and 5.9.

5.5 Discussion

This chapter aimed to investigate the nature of the mixing of different waters within the study catchments both before and after blocking and with increasing scales. The water samples collected were analysed for 15 chemical tracers including pH, conductivity and DOC concentration with the aim of creating an end member mixing model for the water in both the control and experimental catchments. However, after the PCA it is clear that the water in both catchments can be described by a relatively simple mixing trend indicated in Figures 5.8 and 5.9. The PCA indicated that the components with the highest loading were the DOC concentration and pH with the majority of the waters sampled being described by this mixing trend.

As the water moves through the catchment the DOC concentration was seen to decrease and the pH increase. As scale increases the effect of dilution will increase too. This will lead to the reduction in DOC concentration recorded and an increase in pH as waters become less acidic. The sites studied on Cronkley are crossed by bands of limestone which would aid the change in pH recorded on the sites and may also act as a possible source of additional water to the catchment supporting the dilution process.

Chapter 4 described a detailed event analysis to establish whether any changes in physical hydrology were apparent post blocking. The water yield in the drains was found to decrease significantly; however this was not accompanied with a significant increase in the water table to account for the additional water present in the peat indicating that a proportion of the water balance was missing. This chapter has found that a relatively simple mixing model can explain the majority of variation in water composition in the drains and that this does not appear to change post blocking. However, the chemical data has not been able to establish where this missing part of the water balance has gone although it is likely that a proportion of this water is being lost to the underlying bedrock and may be contributed back to the surface water further down the catchment or lost via increased evaporation.

5.6 Conclusions

1. The water within the study catchment can be described by a relatively simple mixing trend rather than a more complex end member mixing model with PCA indicating that DOC concentration and pH are the components with the highest loadings.
2. The water chemistry and mixing is significantly affected by scale but not by the blocking of drains.
3. The chemical data is unable to establish where the missing part of the water balance, indicated in chapter 4, has gone and further research into the loss of water into the bed rock is necessary.

6. Conclusions

6.1 Overall conclusions

6.1.1 Objective 1

To measure the water colour budgets for a nested series of catchments where drains have been blocked in comparison to catchments where drains have not been blocked.

Extensive drainage of UK peatlands has been associated with dehydration of the peat; an increase in water colour; and a loss of carbon storage. It has been considered that the blocking of these drainage channels represents a means of peat restoration and a way of reducing DOC losses to surface waters. This study aimed to assess the effectiveness of drain blocking at both an individual drain scale and at a larger catchment scale (up to 1km^2). A series of blocked and unblocked catchments were studied in Upper Teesdale, Northern England. A detailed sampling programme was undertaken in which a series of blocked drains were studied in the 12 months prior to and post blocking in comparison to a set of drains that were left unblocked.

These stream networks were monitored for both their DOC concentration and export (flux per unit area). The results showed that in terms of DOC concentration a significant decline due to drain-blocking was only found at the first order scale when considered relative to the control catchment and relative to a pre-blocking period. However drain blocking was found to significantly reduce DOC export by reducing water yield in the drain and that the size of this DOC export reduction declines with increasing scale from 9.2% on zero order drains to 2.2% on first order drains. A linear relationship exists between DOC export and water yield at the zero order scale but this relationship becomes more complex at the first order scale as the relationship takes on the characteristics of a mixing model reflecting the effect of changing water sources with scale and providing evidence of the existence of flow bypassing drain blocks.

The results suggest that the effects of drain blocking decrease with increasing scale and that the presence of bypass flow around zero order blockages may limit the success of drain blocking as a method of reducing DOC loss as scale increases.

6.1.2 Objective 2

To assess to what extent DOC is lost from the system by degradation processes.

Chapter 3 aimed to assess the influence of those factors such as DOC degradation, which will cause DOC concentration and export to decline with scale and so would mask the effectiveness of drain blocking if it were present. The effects of photodegradation and biochemical degradation are small; 0.73 mg C/l/day in total. The combined effect of both biochemical and photodegradation although small is still statistically significant. However, it is clear that the reduction in DOC concentration with increasing scale cannot solely be explained by degradation alone and the effects of dilution and water mixing must also be acting on the system.

The size of the influence of DOC degradation in the study catchments may reflect their relatively small spatial area. The control and experimental catchments are 0.750 km^2 and 0.715 km^2 in size respectively and hydrological studies (Chapter 4) of the area have shown that water in the drains has a tendency to move relatively swiftly through the system and out of the catchment meaning there is a limited period of time for the DOC in the water to be subjected to the processes of degradation. Therefore, the influence of degradation may be more obvious when studied at larger catchment scales. However, for a river such as the Tees where the complete travel time from source to mouth is at most only a few days, DOC degradation will still only have a small effect on overall DOC loss meaning that the loss in DOC mass during this period still remains unexplained.

6.1.3 Objective 3

To monitor the water balance and storage through the blocked and control catchments.

The aim of chapter 4 was to assess whether the blocking of peat drains in the study catchments has had a significant effect on the hydrology and water balance of the area via observations of water table depth and analysis of individual rain storm events. The results showed that the water table rose on average from 6cm to 5 cm below the surface. This only slight rise in the water table, although statistically significant, is perhaps explained because the site was naturally wet prior to blocking. Observations of flow and the catchment hydrograph indicate that blocking has slowed the movement of water through the system, however, there is evidence that during very high intensity rainfall events water will top the blockages and move quickly through the catchment creating higher than average peaks in the DOC record. The flow of water over the blockages reflects the small capacity of the peat bog to take in additional water as the peat is naturally close to saturation point. Thus it could be considered that the beneficial effects of blocking i.e. peat rewetting and regeneration will be more visible on drained peats that are naturally drier.

Despite the small change in the depth to the water table there is a considerable decrease in water yield after blocking. The discharge of the blocked drains has been recorded to decrease by a mean value of 16% on the zero order drains and 12% on the first order drains. With a reduction in discharge of this size a larger decrease in the depth to the water table might be expected indicating that more water is being removed from the system in other ways or stored within the catchment. Drain blocking may also have caused increased loss of water via evapotranspiration. However, due to the size of this water yield reduction, evapotranspiration is unlikely to explain all of the water yield reduction. It is possible that the shape and size of the catchment has changed post blocking as water which would have previously exited the catchment via the drains now finds alternative pathways from the system.

The binary logistic regression of the individual rainfall and flow events indicated that blocking had an influence on the probability that a flow event would occur. In both blocked and unblocked catchments at the study site the probability of a rainfall event triggering runoff was controlled by the intensity of the rainfall event, i.e. runoff initiation is controlled by rainfall character and not by antecedent conditions. The soil has very little capacity to take in extra water falling to the ground thus water is likely to runoff through the drainage network. This would mean that the flow events recorded are controlled by the characteristics of the rainfall events rather than the antecedent conditions of the ground which is already at or very close to water storage capacity.

6.1.4 Objective 4

Fingerprinting flow pathways for water and water colour within blocked and unblocked catchments.

Chapter 5 aimed to investigate the nature of the mixing of different waters within the study catchments both before and after blocking, and with increasing scale. After the PCA it is clear that the water in both catchments can be described by a relatively simple mixing trend. The PCA indicated that the components with the highest loading were the DOC concentration and pH with the majority of the waters sampled being described by this mixing trend.

As the water moved through the catchment the DOC concentration was seen to decrease while pH increased. An increase in dilution with increasing scale can explain this reduction in DOC concentration and increase in pH. The sites studied on Cronkley Fell are crossed by bands of limestone which would aid the change in pH recorded on the sites and may also act as a possible source of additional water to the catchment supporting the dilution process.

Chapter 4 described a detailed event analysis routine to establish whether any changes in physical hydrology were apparent post blocking. The water yield in the drains was found to decrease significantly; however this was not accompanied with a considerable increase in the water table to account for the additional water present in the peat indicating that a proportion of the water balance was missing. This chapter has found that a relatively simple mixing model can explain the majority of water in the drains and that this does not appear to change post blocking. However, the chemical data has not been able to establish where this missing part of the water balance has gone although it is likely that a proportion of this water is being lost to the underlying bedrock and may be contributed back to the surface water further down the catchment.

6.1.5 Objective 5

Evaluate to what degree the blocking of drains is beneficial on a large scale across blanket bog and investigating the ideal timescale for monitoring restoration of the peat mass.

This thesis has aimed to assess to what extent the blocking of peat drains has been successful in reducing the DOC export from an upland catchment and how any benefits of drain blocking seen on an individual drain scale transfer to a larger catchment scale. The detail of this study in being able to report a drain-blocking study with a paired catchment approach with both pre- and parallel controls at multiple scales means it is possible to shed light on previous studies. Firstly, if it had only been possible to measure after drain blocking and compare it to an open drain this study would have concluded that for first-order streams drain blocking would increase DOC concentrations. With respect to DOC export, if the blocked drain was compared to its neighbouring unblocked drain, the effect of blocking would have been estimated at 24% reduction for the zero order drains and 12% reduction in DOC export for the first order drains. However, it would not be clear from the data how much of this reduction in DOC export is due to the blocking and how much is due to the natural hydrological variations between the two monitored catchments. Being able to monitor prior to blocking allows a baseline for both the water yield and water colour to be established so that the influence of blocking can be correctly assessed thus a reduced value for the effect of blocking on DOC export can be established at 9.2% for the zero order drains and 2.2% at the first order. Secondly, if this study could only consider the drains before and after drain-blocking without relation to a parallel control it would conclude that in the post blocking year a slight increase in DOC concentration had been recorded at both zero and first order scales. The presence of a control catchment allows this increase to be interpreted as a natural year on year variation and not any effect of blocking. Further, it should be noted that the detail of this study means that it would be possible to demonstrate significant differences in each of these two conjectured comparisons. It is only in the detail of the relative comparison before and after drain blocking that this study can conclude that there was a significant effect and that drain blocking does lower DOC concentration if only in a limited fashion. These findings do mean that previous studies (incl. Worrall et al., 2007a and Gibson et al., 2009) must be treated as limited if not actually misleading. Even with the more detailed analysis included in this study only a small effect of drain-blocking has been found and this decreases with scale suggesting that at larger scales the effect of blocking may be lost.

The small effect of drain-blocking upon DOC concentration is reflected in the changes in DOC export observed, i.e. the dominant affect observed is small when water yield is also considered. The export of DOC was seen to reduce at the zero order scale in a linear fashion with water yield as the blocking of drains causes the water to be held back in the peat thus less DOC is flowing from the system. The decrease in the size of the DOC export reduction upscale gives evidence of a component of bypass flow or ‘leakage’ around the blockage at the zero order scale adding high DOC concentration water to the system down the catchment. The addition of water to the system at the first order channel scale does suggest that bypassing of drain blocks down the slope or on the highest flows is occurring which would suppress the size of the DOC export reduction at this scale.

6.2 Discussion

Previous studies have found the effects of drain blocking to vary from catchment to catchment with studies indicating both increases and decreases in DOC post blocking. Gibson et al. (2009) reported a 20% decrease in DOC export. However, this decrease in DOC export was dominantly caused by a decrease in water yield from the blocked drains rather than a decrease in DOC concentration– although a significant effect, Gibson et al. (2009) observed only a 1% decrease in DOC concentration. This study found a similar effect in that DOC export decreased but that no significant change in actual DOC concentration was recorded. Although a significant decrease in relative DOC concentration (2.5%) was recorded at the first order scale. Wallage et al. (2006) demonstrated a considerable larger effect than that found in this study and Gibson et al. (2009) with DOC concentration decreasing by between 60% and 70% in soil water sampled from piezometers in the vicinity of blocked (5 years prior to monitoring) and unblocked drains at one site in northern England. However this study was limited in that no samples from runoff were measured. Armstrong et al. (2010) combined data from an UK-wide survey of blocked and unblocked drains and found that water colour and DOC concentration was found to be significantly lower in blocked drains with a mean difference of 28% compared to the open drains.

In contrast to this thesis and the studies by Wallage, Gibson and Armstrong; Worrall et al. (2007) found water colour to be slightly higher in blocked drains compared to unblocked drains. However, the work was limited in that monitoring only began 1 month prior to blocking and ceased 8 months after meaning that the results may reflect immediate impacts of disturbance rather than the longer term trend. Equally, Worrall et al. (2007) did show that the flux of DOC would decline post blocking because although DOC concentration rose there was a greater decline in stream flow. Wilson et al. (2011) stated "*that DOC released from blocked drains consisted of lighter, less humic and less decomposed carbon*". Wilson et al. (2011) found that whilst concentrations of DOC showed slight increases in drains and streams after blocking, instantaneous yields of both DOC and POC decreased over the first year post-blocking. Waddington et al. (2008) found that DOC concentration in drains in Canada increased after restoration, however, the drains in the study were only hydrologically blocked at one end and were infilled with loose vegetation and covered with peat meaning that comparison with the UK studies is limited.

This study found the effects of blocking on DOC concentration to be very small with no significant decrease in actual DOC concentration being recorded and a 2.5% significant decrease in relative DOC concentration being recorded at the first order scale. This small decrease has been attributed in chapter 2 and chapter 4 to the relatively small change in the water table recorded post blocking. The sites on Cronkley Fell were naturally very wet at the start of the experiment and water table was found to move on average from 6cm to 5cm below the surface. Worrall et al. (in review) have shown a statistical decline in soil and runoff water DOC concentration upon cutting or burning of *Calluna vulgaris* on a peat soil and have associated this decline with change in water table depth with lower DOC concentrations occurring as water tables become shallow, but that the average change in water table depth was 40 cm. In addition Ramchunder et al. (2012) and Guo et al. (2012) found that the effects of drain blocking on DOC concentration build cumulatively over time. If this is the case the monitoring on Cronkley Fell may not have been of long enough duration to demonstrate any larger decrease in DOC concentration.

One of the important questions that this thesis intended to answer is whether the effects of blocking seen at the individual drain scale can be transferred to larger catchment scales and how large an influence those factors outlined in chapter 1 such as bypass flow, in stream DOC loss processes e.g. DOC degradation, and dilution will have on the efficiency of drain blocking. The study found that DOC degradation was small; 0.73 mg C/l/day in total yet the change in DOC concentration from the zero order drains to the first order drains was approximately 20 mg/l. It is thus clear that DOC degradation cannot explain the change in DOC concentration alone and that dilution effects and bypass flow are likely to be occurring. The size of the DOC degradation effect recorded at Cronkley is considerable smaller than those found in the literature. Worrall et al. (2006) estimated an average mass loss of 27% from a sub 1 km^2 catchment to an 11.4 km^2 catchment, an equivalent export of between 4 and 7.4 Mg C/km2/yr. Worrall and Burt (2004) found an average net loss of 40% for the River Tees from source to outlet. The study catchments on Cronkley Fell are considered to be water source dominated with water being added to the catchment from external sources. This may mask the effects of in stream DOC loss and explain the small levels recorded in this study.

The study found a significant decrease in DOC export post blocking and that this decrease can on the whole be related to a significant decrease in water export.

Yet this decrease in water export was not accompanied by a major increase in the water table to account for the additional water present in the peat indicating that a proportion of the water balance was missing. Chemical tracing experiments in chapter 5 were unable to establish where this missing part of the water balance had gone.

It was found that the size of the reduction in DOC export and water export decreased with increasing scale. It is postulated that this decrease in the size of the DOC export reduction is due to a combination of bypass flow around the zero order blockages and additional spatially variable external water sources, adding water to the first order drains, suppressing the impact of the DOC export reduction. The presence of any bypass flow or external water sources will reduce the efficiency of any blocking. This addition of water at the larger first order scale would also explain the dilution effect seen in the decrease of the DOC concentration from zero to first order. This additional water is likely to come from a number of sources such as runoff, soil water, ground water and through soil pipes. The addition of this missing water is demonstrated schematically in Figure 6.1.

The dehydration of peat bogs after drainage has been linked to changes in the soil structure and an increase in flow in soil pipes (Holden et al., 2005a). Alternative flow pathways such as soil pipes are created as the soil cracks and degrades while drying due to the increased drainage (Holden and Burt, 2002 a, b). Holden et al. (2007) states "*that this change in soil structure is important for the hydrology, water quality and ecology in moorlands when attempts are made to rewet the soil after drain blocking*". Several studies have indicated that flow through soil pipes forms a notable large part of the water balance. A study by Jones and Crane (1984) of a peat moor in Wales reported the movement of water through soil pipes accounted for 50% of total streamflow. Holden and Burt (2002c) determined that for a blanket bog in the north Pennines flow in soil pipes accounted around 10% of total streamflow. The extent of soil piping and the size of the individual soil pipes in blanket peats have been shown to increase over time (Holden et al., 2006).

The large extent of soil piping in drained peats must be considered when drain blocking management strategies are employed. Holden et al. (2007) states that "*it may be that damming the drains simply allows more water to enter the pipe networks*

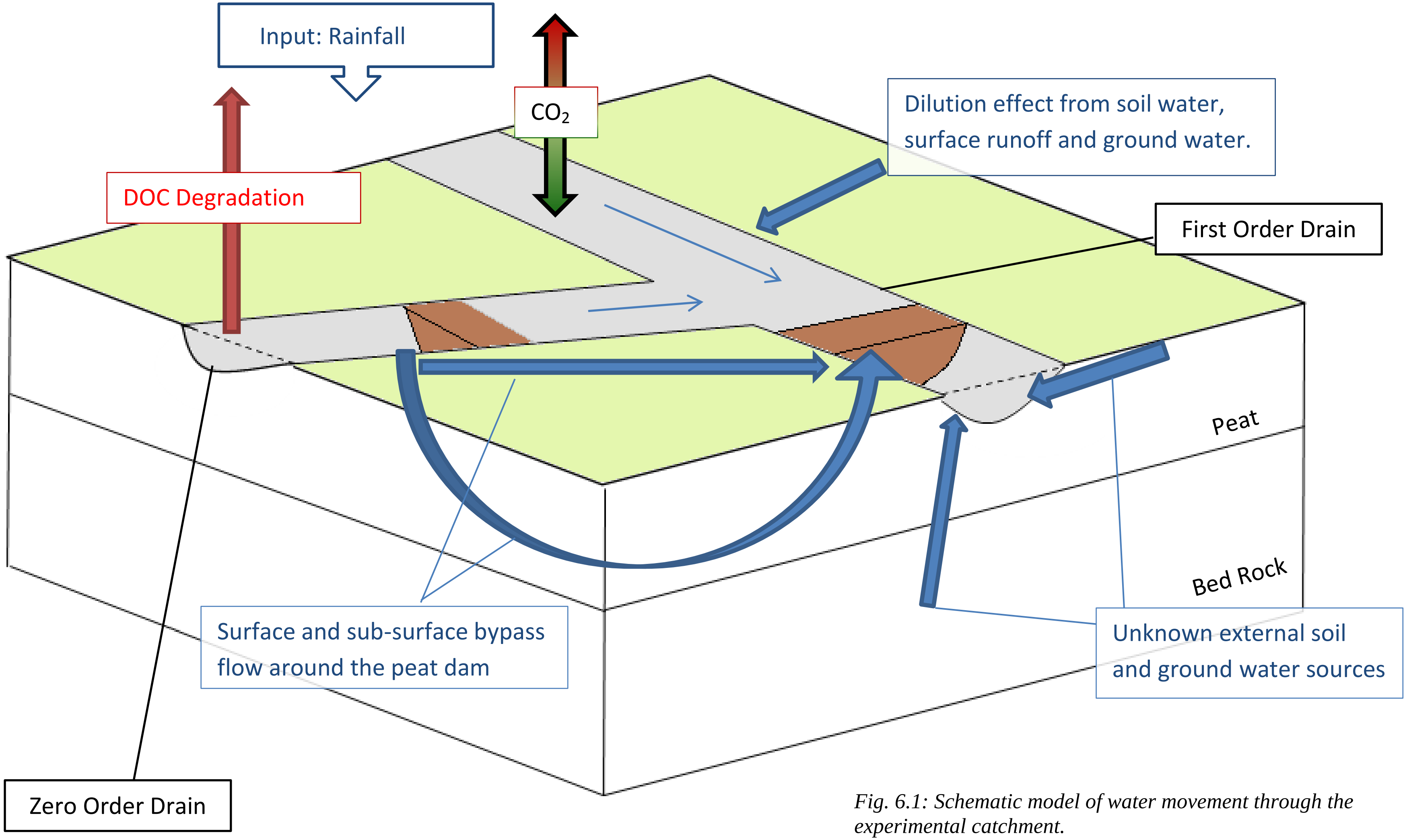


Fig. 6.1: Schematic model of water movement through the experimental catchment.

that have openings on drain floors and sides". The presence of soil pipes in the study catchments at Cronkley Fell would explain why the reduction in DOC export is smaller at the first order scale and help locate the missing part of the water balance indicated by the hydrological data. The presence of any bypass flow whether by soil pipes, run off or soil through flow would have important implications for drain blocking efficiency and for the study of the success of drain blocking.

6.3 Data Limitations

It is acknowledged that there are some limitations inherent in the methods and data used in this study. Firstly, in terms of the analysis protocols used. Due to the large number of samples collected in the drain sampling campaigns it was not possible to directly analyse DOC concentration on each sample and therefore absorbance was used as a proxy for DOC. Regular calibration experiments for this relationship were carried out which indicated that the adoption of individual calibration curves for each sites was appropriate for these data.

The data collected was also limited by the nature of the environment in which this study was conducted. All nine monitoring sites were equipped with a range of scientific instrumentation including automatic water samplers and dataloggers set up to monitor flow, conductivity and a range of weather parameters. Due to the extreme nature of weather conditions at the localities the breakdown of equipment at certain times is somewhat inevitable. The control panels on the automatic water samples along with wiring in the data loggers are sensitive to water damage. Measures were taken to reduce the impact of water damage, for example, water absorbent silica packs were inserted inside datalogger boxes and then placed along with the auto-samplers at as greater distance from the drains as possible. However heavy snow is common in the area and equipment was often buried under approximately 30 cm of snow during the winter. This meant that access to the sites could not occur to rescue faulty kit and also led to gaps in the data. These gaps in the data were then filled by the extrapolation of data either from the previous year or from similar sites across upper Teesdale.

In addition to snow the freezing of drains in winter reduced equipment reliability. Pressure transducers used to calculate flow were attached directly to the weir plates. If the drain water was to freeze at the same water depth as the pressure transducer this would cause a significant pressure increase in the probe leading in some cases to irreparable damage. Also water in the autosampler pipes is liable to freeze in these conditions, leading to lost water samples, although in the majority of cases leading to no damage to the equipment itself. This again led to gaps in the data record.

The poor weather also led to a delay in the drain blocking. Drains in the experimental catchment were due to be blocked in December 2008 however due to high snow levels the drains were not blocked until March 2009. This time of year is normally the start of the spring flush period and the increased water yield and snow melt may have affected the levels of DOC export recorded immediately after blocking. Monitoring did however continue for 12 months following blocking so any inaccuracies in the data caused by the timing of the blocking should cancel out over the year

The findings of this study are also limited in that they can only comment on the effects of blocking for the first 12 months post intervention and not any long term effects. Ramchunder et al. (2012) and Guo et al. (2012) found that the effects of drain blocking build cumulatively over time and that longer term monitoring is essential to assess the true success of any blocking. However this study did find no significant interaction between month and blocking when ANOVA was performed on the water yield and water export indicating that the effects of blocking, on the hydrology at least, appear to be immediate rather than cumulative. This study also did not consider the change in vegetation over monitored period and any affect that this may have had on DOC loss. Dixon et al. (2011) has demonstrated a relationship between the age of heather and the levels of DOC in soil water dipwells. It is consider that due to the short length of the study, 12 months monitoring before blocking and 12 months post blocking, that the growth of heather during this period would have only a slight effect on the level of DOC recorded leaving the catchment however changes in vegetation should be considered in longer term studies of drain blocking.

6.4 General Conclusions

With reference to all the above objectives, the key findings of this work can therefore be summarised as follows:

1. This study found a significant decline in relative DOC concentration at the first order scale post blocking of 2.5%. A decrease in DOC concentration is recorded as water flows from the zero to the first order in the same catchment indicating the importance of dilution effects in the catchments.
2. The blocking of peat drains does significantly decrease the export of DOC from peat drains; however this is largely achieved by decreasing water yield. The size of the DOC export reduction caused by drain blocking is seen to decrease as scale increases providing evidence for the existence of bypass flow around the zero order drain blockages.
3. Biochemical and photodegradation are found to have only a small reducing influence, approximately 0.73 mg C/l/day, on DOC moving from zero to first order drains. It is clear that the combined effects of DOC degradation cannot solely explain the decrease in DOC concentration seen from zero to first order drains in the study catchments. Also there was no observed effect of drain-blocking on either pathway.
4. Blocking had a significant although small impact on the water table of the area with the peat bog being natural very wet such that when blocking did occur the soil had little capacity to take in additional water. Water yield however is seen to decrease post blocking indicating that water is being lost from the system. This loss cannot currently be explained.
5. The water chemistry within the study catchment can be described by a relatively simple mixing trend rather than a more complex end member mixing model with PCA indicating that DOC concentration and pH are the components with the highest loadings. The water chemistry and mixing is significantly affected by scale but not by the blocking of drains.

6.5 Recommendations for future work

The findings of this study and its limitations can be used to direct a number of future research objectives. This study has demonstrated that a small if significant effect of DOC does exist post blocking for this study site, therefore, two questions arise – what is causing this change? and why is not larger? The decrease in DOC concentration could be due to a balance between enzymic-latch effects, or sulphide-oxidation effects causing increases in DOC production or solubility upon the rise of the water table against reduced DOC production due to reduced depth of the aerobic zone. All of these effects will be greater with a greater change in the depth of the water table and indeed the small magnitude of the effect observed in this study may well be explained by the fact that the average change in depth to water table for the study was only 1 cm from 6cm depth to 5cm depth, i.e. the change in water table was very slight. As stated above Worrall et al. (in review) have shown a statistical decline in soil and runoff water DOC concentration upon cutting or burning of *Calluna vulgaris* on a peat soil and have associated this decline with a change in water table depth with lower DOC concentrations occurring as water tables become shallow, but that the average change in water table depth was 40 cm. Therefore, there is a need to compare the findings of this study with one from a naturally drier low lying peat bog or from a study where alternative management strategies have been employed.

There is a very slight change in the depth to the water table (on average 1cm post blocking) however analysis of the drain discharge did show a significantly larger decrease (16% on the zero order drains and 12% on the first order drains). This difference indicates that a component of the water balance is being lost which cannot be accounted for by the chemical analysis performed and may in turn mean that DOC is being lost from the system. Water moving though the peat will not only flow laterally through the system but due to vertical hydraulic head move downwards in to the underlying bedrock. It is hypothesised that a component of the water balance is being lost to this underlying geology. It is important that future research should be directed towards finding this missing component of the water balance potential by introducing artificial tracers in to the system and tracing there movement through high intensity monitoring methods.

The sole focus of this study on water colour leaving upland catchments means that other aspects of the carbon cycle of peatlands are not addressed. As described in chapter 1 several studies have identified changes in other aspects of the carbon budget of peats following water table rise, with CO_2 exports generally decreasing and CH_4 exports increasing. Construction of a total carbon budget for the study catchments at Cronkley Fell is beyond the scope of this study but works towards such a goal is underway at the University of Durham; the data from this project will form an important component of this as DOC has been shown to be the dominant form of carbon export.

7. Bibliography

Adger A, Cox CS, Jones CA. 2004. Enhancement of coagulation control using the streaming current detector. Bioprocess and Biosystems Engineering **27**(5), 349-357.

Aitkenhead JA, Hope D, Billet MF. 1999. The relationship between dissolved organic carbon in stream water and soil organic carbon pools at different spatial scales. Hydrological Processes **13**, 1289-1302.

Armstrong A, Holden J, Kay P, Foulger M, Gledhill S, McDonald AT. 2009. Drain-blocking techniques on blanket peat: a framework for best practice. Journal of Environment Management **90**(11), 3512–9.

Armstrong A, Holden J, Kay P, Francis B, Foulger M, Gledhill S, McDonald AT, Walker A. 2010. The impact of peatland drain-blocking on dissolved organic carbon loss and discolouration of water; results from a national survey. Journal of Hydrology **381**, 112-120.

Baden W, Eggelsmann R. 1970. Hydrological budget of high peat bogs in the Atlantic region. Proceedings of the third International Peat Congress, 1968. Department of Energy, Mines and Resources, Ottawa, Quebec, 260-311.

Barlett RJ, Ross DS. 1988. Colorimetric determination of oxidizable carbon in acid soil solutions. Soil Science Society of America Journal **52**, 1191-1192.

Bengtson H. 2010. Open Channel Flow Measurement 4: the V Notch Weir. (http://www.brighthub.com/engineering/civil/articles/65701.aspx retrieved 11th August 2011

Birch HF. 1958. The effect of soil drying on humus decomposition and nitrogen availability. Plant and Soil **10** (1), 9-31.

Birch HF. 1960. Nitrification in soils after different periods of dryness. Plant and Soil **12** (1), 81-96.

Bouma J. 1990. Using morphic expressions for macropores to improve soil physical analyses of field soils. Geoderma **46**, 3-11.

Breuer WS, Abernathy AR, Paynter MJB. 1997. Oxygen consumption by freshwater sediments. Water Research **11**, 471-473.

Brinkmann,T, Hörsch, P, Sartorius, D. 2003. Photoformation of Low-Molecular-Weight Organic Acids from Brown Water Dissolved Organic Matter. Environmental Science Technology **37** (18),4190–4198

Burke W. 1975. Effect of drainage on hydrology of blanket bog. Irish Journal of Agricultural Research **14**(2), 142-162

Bursil D. 2001. Drinking water treatment-understanding the processes and meeting the challenges. Water Science and Technology: Water Supply **1**(1), 1-7.

Burt T, Adamson JK, Lane AMJ. 1998. Long term rainfall and streamflow records for north central England: Putting the environmental change network site at Moor House, Upper Teesdale, in context. Hydrological Science Journal **43**(5), 775-787.

Butler JN. 1982. Carbon dioxide equilibrium and its applications, Addison- Wesley, Reading, MA.

Campbell Scientific. 2007. Index of products and technical notes, http://www.campbellsci.co.uk/index

Cannell MGR, Milne R, Hargreaves KJ, Brown TAW, Cruickshank MM, Bradley RI. 1999. National inventories of terrestrial carbon sources and sinks: the UK experience. Climate Change **42**, 505–30.

Chatfield C, Collins AJ. 1980. Introduction to Multivariate Analysis. London, Chapman and Hall.

Chrisopher N, Hooper RP. 1992. Multivariate analysis of stream water chemical data- The use of principal component analysis for the end member mixing problem. Water Resources Research **28**(1), 99-107.

Clark JM, Chapman PJ, Adamson JK, Lane SN. 2005. Influence of drought-induced acidification on the mobility of dissolved organic carbon in peat soils. Global Change Biology **11**(5), 791–809.

Clark JM, Bottrell SH, Evans CD, Monteith DT, Bartlett R, Rose R, Newton RJ, Chapman PJ. 2010. The importance of the relationship between scale and process in understanding long-term DOC dynamics. Science of the Total Environment **408**, 2768–2775

Clausen JC. 1980. The quality of runoff from natural and disturbed Minnesota peatlands. The role of peatlands in a world of limited resources, energy, food, fibre and natural areas, 6th internation peat congress, Minnesota, International Peat Society, 523-532.

Clow DW, Drever JI. 1996. Weathering rate as a function of flow through an alpine soil. Chemical Geology **132**, 131-141.

Cole JJ, Caranco NE. 1998. Atmospheric exchange of carbon dioxide in a low wind oligotrophic lake measured by the addition of SF6. American Society of Limology and Oceanography **43**, 647-656.

Cole L, Bardgett RD, Ineson P, Adamson JK. 2002. Relationships between enchytraeid worms (Oligochaeta), climate change and the release of DOC from blanket peat in Northern England. Soil Biology and Biochemistry **34**(5), 599-607.

Cooper A, Murray R, McCann T. 1991. The environmental effects of blanket peat eeploitation. Coleraine: University of Ulster.

Dail Eireann. 1998. Dail Eireann- volume 487-26 February, 1998 Written Answers-Raised bog conservation.

Davis RE. 1991. Lagrangian Ocean Studies. Annual Review of Fluid Mechanics **23**, 43–64

Davis AMC. 2005. Back to basics: Applications of principal component analysis. Spectroscopy Europe **17**(2), 30-31.

Dawson J, Billet MF, Neal C, Hill S. 2002. A comparison of particulate, dissolved and gaseous carbon in two contrasting upland streams in the UK. Journal of Hydrology **257** (1-4), 226-246.

De Vries A, Klavers HC. 1994. Riverine fluxes of pollutants: monitoring strategies first, calculation methods second. European Water Pollution Contributions **4**, 12-17.

Dixon S. 2011. Controls on carbon cycling in upland blanket peat soils. PhD Thesis. University of Durham.

Driscoll CT, Driscoll KM, Roy KM, Mitchell ML. 2003. Chemical response of lakes in the Adirondack region of New York to declines in acidic deposition. Environmental Science and Technology **37**, 2036-2042.

Duan N. 1983. Smearing estimate: a non-parametric retransformation method. Journal of American Statistical Society **78**, 605-610.

Efron B, Tibshirani R. 1986. Bootstrap methods for standard errors, confidence intervals and other measures of statistical accuracy. Statistical Science **1**(1), 54-77.

Eggelsmann R. 1971. On hydrological influence of a bog. Telma **1**(1), 37-38.

Essl F, Dullinger S, Moser D, Rabitsch W, Kleinbauer I. 2012. Vulnerability of mires under climate change: implications for nature conservation and climate change adaptation. Biodiversity and Conservation **21** (3), 655-669

Evans MG, Burt TP, Holden J, Adamson JK. 1999. Runoff generation and water rable fluctuations in blanket peat: evidence from UK data spanning the dry summer of 1995. Journal of Hydrology **221**(3-4), 141-160.

Evans CD, Monteith DT. 2001. Chemical trends at lakes and streams in the UK acid waters monitoring network, 1988-2000: evidence for recent recovery at a national scale. Hydrology and Earth Systems Science **5**, 351-366.

Evans CD, Monteith DT, Cooper DM. 2005. Long term increases in surface water dissolved organic carbon: Observations, possible causes and environmental impacts. Environmental Pollution **137**(1), 55-71.

Evans M, Warburton, J**.** 2005. Sediment budget for an eroding peat-moorland catchment in northern England. Earth Surface Processes and Landforms **30**: 557-577.

Evans MG, Warburton J, Yang J. 2006. Sediment budgets for eroding blanket peat catchments: global and local implications of upland organic sediment budgets. Geomorphology **79**(1-2), 45-57.

EU Directives 80/778/EEC, 2008.

Fearings DA, Banks J, Guyetand S, Eroles CM, Jefferson B, Wilson D, Hillis P, Campbell AT, Parsons SA. 2004. Combination of ferric and MIEX ® for the treatment of a humic rich water. Water Research **38**(10), 2551-2558.

Fleck JA, Bossio DA, Fujii R. 2004. Dissolved organic carbon and disinfection by-product precursor release from managed peat soils. Journal of Environmental Quality **33**, 465-475.

Forsberg C. 1992. Will an increased Greenhouse Impact in Fennoscandia give rise to more humic and coloured lakes. Hydrobiologia **229**, 51-58.

Freeman C, Evans CD, Montieth DT, Reynolds B, Fenner N. 2001a. Export of Organic carbon from peat soils. Nature **412**, 785-786.

Freeman C, Ostle N, Kang H. 2001b. An enzyme latch on a global carbon store- a shortage of oxygen locks up carbon in peatlands by restraining a single enzyme. Nature **409**, 149.

Freeman C, Ostle NJ, Fenner N, Kang H. 2004. A regulatory role for phenol oxidase during decomposition in peatlands. Soil Biology & Biochemistry **36**(10), 1663-1667.

Freeman C, Fenner N, Ostle NJ, Kang H. 2004. Export of dissolved organic carbon from peatlands under elevated carbon dioxide level. Nature **430**, 195-198

Fullen MA. 1983. Some changes in air temperature and wind velocity after burning of heather (Calluna vulgaris) moor and their relation to moorland surface processes. Naturalist **108**, 17–24.

Garnett MH, Ineson P, Stevenson AC. 2000. Effects of burning and grazing on carbon sequestration in a Pennine blanket bog, UK. Holocene **10** 729–36.

Gibson HS. 2006. Sources and management of water colour in the River Tees. PhD thesis, University of Durham

Gibson HS, Worrall F, Burt TP, Adamson K. 2009. DOC budgets of drained peat catchments: implications for DOC production in peat soils. Hydrological Processes **23**, 1901-1911.

Glatzel S, Kalbitz K, Dalva M, Moore T. 2003. Dissolved organic matter properties and their relationship to carbon dioxide efflux from restored peat bogs. Geoderma **113**, 397–411.

Glatzel S, Ruiz P, Jurasinski G. 2012. Methane release from a rewetted coastal fen in north east Germany. Geophysical Research Abstracts, EGU General Assembly 2012 **14**.

Gorham E. 1991. Northern peatlands: Role in the carbon cycle and probable responses to climatic warming. Ecological Applications **1**, 182-195.

Grand-Clement E, Luscombe D, Le Feuvre N, Smith D, Anderson K, Brazier RE. 2012. Effects of peatland drainage on water quality: a case study of the shallow blanket bogs of Exmoor, UK. EGU General Assembly 2012, 789.

Graneli, Wilhelm, Mans, Lindell, Tranvik.1996. Photo-oxidative production of dissolved inorganic carbon in lakes of different humic content. Limnology Oceanography **41**, 698.

Grieve IC. 1990. Seasonal, Hydrological and Land management factors controlling DOC concentrations in the Loch Fleet catchments, Southwest Scotland. Hydrological Processes **16**(16), 3113-3130.

Guo YD, Song CC, Wang LL. 2012. Impact of natural wetland degradation on dissolved carbon dynamics in the Sanjiang Plain, Northeastern China. Journal of Hydrology **398**(1-2), 26-32.

Haag I, Westrich B. 2002. Processess governing river water quality identified by principal component analysis. Hydrological Processes **4**(3), 231-239

Hatala JA, Detto M, Sonnentag O, Deveral SJ, Verfaillie J, Baldocchi DD. 2012. Greenhouse gas fluxes from drained and flooded agricultural peatlands in the Sacramento-San Joaquin Delta. Agriculture, Ecosystems and Environment **150**, 1-18

Hejzlar J, Dubrovsky M, Buchtele J, Ruzicka M. 2003. The apparent and potential effects of climate change on the inferred concentration of dissolved organic matter in a temperate stream (the Malse River South Bohemia). Science of the Total Environment **310**, 143-152.

Heppell CM, Worrall F, Burt TP, Williams RJ. 2002. A classification of drainage and macropore flow in an agricultural catchment. Hydrological Processes **16**, 27-46.

HMSO. 1988. 5 day biochemical oxygen demand (BOD5). Methods for the examination of waters and associated materials. HMSO, London

Holden J, Burt TP. 2002a. Infiltration, runoff and sediment production in blanket peat catchments: implications of rainfall simulation experiments. Hydrological Process **16**(13), 2537-2557.

Holden J, Burt TP. 2002b. Laboratory experiments on drought and runoff in blanket peat. European Journal of Soil Science **53**(4), 675-689.

Holden J, Burt TP. 2002c. Piping and pipeflow in a deep peat catchment. Catena **48**(3), 163-199.

Holden J, Burt TP. 2003a. Hydrological studies on blanket peat: the significance of the acrotelm- catotelm model. Journal of Ecology **91**(1), 86-102.

Holden J, Burt TP. 2003b. Runoff production in blanket peat covered catchments. Water Resources Research **39**(7), art. no. 1191

Holden J, Chapmen PJ, Labadz JC. 2004. Artificial drainage of peatlands: hydrological and hydrochemical process and wetland restoration. Progress in Physical Geography **28**(1), 95-123.

Holden J. Bosanko NR, Gasgcoign M. 2005. Erosion caused by surface land drains in upland peatlands and impact of remediation strategies. European Geophysical Union General Assembly. Vienna, Austria, Geophysical Research Abstracts 7.

Holden J. 2005a. Controls of soil pipe frequency in upland blanket peat. Journal of Geophysical Research **110**

Holden J, Evans MG, Burt TP, Horton M. 2006. Impact of land drainage on peatland hydrology. Journal of Environmental Quality **35**(5), 1764-1778.

Holden J, Shotbolt L, Bonn A, Burt TP, Chapman PJ, Dougil AJ, Fraser EDG, Hubacek K, Irvine B, Kirkby MJ, Reed MS, Prell C, Stagl S, Stringer LC, Turner A, Worrall F. 2007. Environmental change in moorland landscapes. Earth Science Reviews **82**, 75-100.

Höll BS, Fiedler S, Jungkunst HF, Kalbitz K, Freibauer A, Drösler M, Stahr K. 2009. Characteristics of dissolved organic matter following 20 years of peatland restoration. Science of the Total Environment **408**, 78–83

Hooijer A, Silvius M, Wosten H, Page S. 2006. Peat- CO2, Assessment of CO2 emissions from drained peatlands in SE Asia. Delft Hydraulics Report Q3943 (2006)

Hooper RP. 2001. Applying the scientific method to small catchment studies: A review of the Panola mountain experience. Hydrological Processes **15**, 2039-2050.

Hooper RP. 2003. Diagnostic tools for mixing models of stream water chemistry. Water Resources Research **39**(3) 1055.

Hope D, Billet MF, Cresser MS. 1994. A review of the export of carbon in river water: fluxes and processes. Environmental Pollution **84**, 301-324.

Hotelling H. 1933. Analysis of a complex of statistical variables into principal components. Journal of Educational Psychology **24**, 417-41, 498-520.

Huttunen JT, Nykanen H, Turunen J, Martikainen PJ. 2003. Methane emissions from natural peatlands in the northern boreal zone in Finland, Fennoscandia. Atmospheric Environment **37**, 147–151.

Hsu CH, Jeng WL, Chang RM, Chien LC, Han BC. 2001. Estimation of potential lifetime cancer risk for trihalomethanes from consuming chlorinated drinking water in Taiwan. Environmental Research **85**(2), 77-82.

Imeson AC. 1971. Heather burning and soil erosion on the North Yorkshire moors. Journal Applied Ecology **8**, 537–42.

Ingram HAP. 1978. Soil in layers in mires- Function and terminology. Journal of Soil Sciences **29**(2), 224-227

ISO. 1980. Water flow measurement in open channels using weir and venture flumes- Part 1: Thin plate weirs. ISO 1438/1-1980(E)

ISO. 1990. Water quality sampling. Part 1: Guidelines on the design of sampling programmes. International standard ISO 5667-1, International organisation for standardisation Geneva.

ISO. 1990. Water quality sampling. Part 2: Guidelines on sampling techniques. International standard ISO 5667-2, International organisation for standardisation, Geneva.

ISO. 1990. Water quality sampling. Part 3: Guidelines on the preservation and handling of samples. International standard ISO 5667-3, International organisation for standardisation, Geneva.

ISO. 1990. Water quality- Determination of biochemical oxygen demand after 5 days (BOD5), dilution and seeding method. International standard ISO 5815, International organisation for standardisation, Geneva.

Joensuu S, Ahti E, Vuollekoski M. 2002. Effect of ditch network maintenance on the chemistry of run-off water from peatland forests. Scandinavian Journal of Forest Research **17**, 238-247.

Jones JAA, Cranes FG. 1984. Pipeflow and pipe erosion in the Maesnant experimental catchment. In Burt TP, Walling DE. (Eds), Catchment experiments in fluvial geomorphology. Geo Books, Norwich, 55-72.

Jones JAA. 2004. Implications of natural soil piping for basin management in upland Britain. Land Degradation and Development **15**(3) 325-349.

Jones JB, Mulholland PJ. 1998. Carbon dioxide variation in a hardwood forest stream: an integrative measure of whole catchment soil respiration. Ecosystems **1**, 183–196.

Joosten H. 1997. European mires: a preliminary status report. International mire cons. Group members newsletter. 3, 10-13.

Komulainen VM, Tuittila ES, Vassander H, Laine J. 1999. Restration of drained peatlands in southern Finland: initial effects on vegetation change and CO2 balance. Journal of Applied Ecology **36**(5), 634-648.

Kopacek J, Hejzlar J, Kana J, Porcal P, Klementova S. 2003. Photochemical, chemical, and biological transformations of dissolved organic carbon and its effect on alkalinity production in acidified lakes. Limnology and Oceanography **48**(1), 106–117.

Krug EC, Frink CR. 1983. Acid rain on acid soil- a new perspective. Science **221**(4610), 520-525.

Lange H, Morris PH**,** Williamson CE. 2003. Solar ultraviolet photodegradation of DOC may stimulate freshwater food webs. Journal of Plankton Research. **25**(1) 111-117

Larson JH, Frost PC, Lodge DM, Lamberti GA. 2007. Photodegradation of dissolved organic matter in forested streams of the northern Great Lakes region. Journal of the North American Benthological Society **26**(3), 416-425

Limpens J. 2008. Peatlands and the carbon cycle: from local processes to global implications- a synthesis. Biogeosciences **5,** 1475-1491.

Littlewood IG. 1995. Hydrological Regimes, Sampling stratagies and Assement of errors in mass load estimates for United Kingdom rivers. Environment International **21**(2), 211-220.

Lumsdon. 2001. European Journal Soil Science 55, 271

Mallik AU, Fitzpatrick EA. 1996. Thin section studies of Calluna heathland soils subject to prescribed burning. Soil Use Manage **12**, 143–9.

Manly BFJ. 1986. Multivariate Statistical Methods: A Primer, Third Edition. Chapman & Hall Statistics Texts

McDonald AT, Mitchell G, Naden PS, Martin DSJ. 1991. Discoloured water investigations. Report to Yorkshire Water, University of Leeds.

McKnight D, Thurman EM, Wershaw RL, Hemond H. 1985. Biogeochemistry of Aquatic Humic Substances in Thoreau Bog, Concord, Massachusetts. Ecology **66**(4), 1339-1352.

McKnight D, Benkala K, Zellweger G., Aiken G, Feder G, Thorn K. 1992. Sorption of dissolved organic carbon by hydrous aluminum and iron oxides occurring at the confluence of Deer Creek with the Snake River, Summit County, Colorado. Environmental Science and Technology **26**(7), 1388- 1396.

Meybeck M. 1993. Riverine transport of atmospheric carbon: Sources, Global typology and budget. Water, Air and Soil pollution **70**, 443.

Milne R, Brown TA. 1997. Carbon in vegetation and soils of Great Britain. Journal of Environmental Management **49**, 413-433.

Mitchell G, McDonald AT. 1992. Discolouration of water by peat following induced drought and rainfall simulation. Water Research **26**(3), 321-326.

Mitchell G, McDonald AT. 1995. Catchment characterization as a tool for upland water quality management. Journal of Environmental Management **44**(1), 83-95.

Monteith DT, JStoddard JL, Evans CD, De Wit HA, Forsius M, Hogasen T, Wilander A, Skjelkvale BL, Jeffries DS, Vuorenmaa J, Keller B, Kopacek J, Vesely J. 2007. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. Nature **450**, 537–541.

Moran MA, Zepp RG. 1997. Role of photoreactions in the formation of biologically labile compounds from dissolved organic matter. Limnology and Oceanography **42**(6), 1307–1316.

Moran MA, Sheldon WM, Zepp. 2000. Carbon loss and optical property changes during long term photochemical and biological degradation of estuarine dissolved organic matter. Limnology and Oceanography **45**, 1254-1264.

Morris RD, Audel AM, Angelillo IF, Chalmers TC, Mosteller F. 1992. Chlorination, Chlorination byproducts and cancer- a Metaanalysis. American Journal of Public Health **82**(7), 955-963

Mostofa KMG, Yoshioka T, Konohira E, Tanoue E. 2007. Photodegradation of fluorescent dissolved organic matter in river waters. Geochemical Journal **41**, 323-331.

Mostofa KMG, Honda Y, Sakugawa H. 2005. Dynamics and optical nature of fluorescent dissolved organic matter in river waters. Geochemical Journal 39, 257-271.

Naden PS, McDonald AT. 1989. Statistical modelling of water colour in the uplands-the upper Nidd catchment 1979-1987. Environmental Pollution **60**(1-2), 141-163.

Neal C, Hill S. 1994. Dissolved inorganic and organic carbon in moorland and forest streams: Plynlimon, Mid-Wales. Journal of Hydrology **153**, 231-243.

National council of the paper industry for air and stream improvement, Inc. 1982. A review of ultimate BOD and its kinetic formulation for pulp and paper mill effluents. Tech. Bull. No. **382**, New York.

Northumbrian Water Ltd. 2010. www.nwl.co.uk/Teeswatercolourproject.aspx retrived 13th December 2010.

Nykanen H, Alm J, Lang K, Silvole J, Martikainen PJ. 1995. Emissions of CH_4, N_2O and CO_2 from a virgin fen and a fen drained for grassland in Finland. Journal of Biogeography **22**, 351–357

Obernosterer I, Benner R. 2004. Competition between biological and photochemical processes in the mineralization of dissolved organic carbon. Limnology and Oceanography **49**, 117.

Olive LJ, Rieger WA. 1988. An examination of the role of sampling strategies in the study of suspended sediment transport. Sediment budgets, Porto Alegre, IAHS.

Osborn TJ, Hulme M. 2002. Evidence for trends in heavy rainfall events over the UK. Philosphical Transactions of the Royal Society of London Series a-Mathematical Physical and Engineering Science **360**(1796), 1313-1325.

Packham RF. 1964. Studies of organic colour in natural water, Proceedings of Society Water Treatment Examination **13,** 316-334

Pastor, J., Solin, J., Bridgham, S. D., Updegraff, K., Harth, C., Weishampel, P., Dewey, B. 2003. Global warming and the export of dissolved organic carbon from boreal peatlands. Oikos **100**, 380–386.

Pearson K. 1901. On lines and planes of closest fit to a system of points in space. Philosophical Magazine **2**, 557-572.

Petersen WL, Bertine L, Callies U, Zorita E. 2001. Process identification by principal component analysis of river water-quality data. Ecological Modelling **138**(1-3), 193-213.

Petrone R, Waddington JM, Price JS. 2001. Ecosystem scale evapotranspiration and net CO2 exchange from a restored peatland. Hydrological Processes **15**(14), 2839-2845.

Phillips JM, Webb BW, Walling DE, Leeks GJL. 1999. Estimating the suspended sediment loads of rivers in the LOIS study area using infrequent samples. Hydrological Processes **13**(7), 1035-1050.

Pinol J, Avila A. 1992. Streamwater pH Alkalinity, PCO2 and discharge relationships in some forested Mediterranean catchments. Journal of Hydrology 131(1-4), 205-225.

Radcliffe DA, Oswald PH. 1988. The flow country: the peatlands of Caithness and Sutherland. Nature Conservancy Council, Peterborough.

Ramchunder SJ, Brown LE, Holden J. 2012. Catchment-scale peatland restoration benefits stream ecosystem biodiversity. Journal of Applied Ecology **49**(1), 182-191.

Reeve RN. 1994. Environmental Analysis. John Wiley and Sons, Chichester.

Robinson M. 1985. The hydrological effects of moorland gripping: a reappraisal of Moor House research. Journal of Environmental Management **21**, 205-211.

Rowson J. 2007. Carbon Emissions from Managed Upland Peat. PhD thesis, University of Durham.

Rycroft DW, Williams DJA, Ingram HAP. 1975. The transmission of water through peat: I. Review. The Journal of Ecology **63**(2), 535-556.

Sarmiento JL, Sundquist ET. 1992. Revised budget for the oceanic uptake of anthropogenic carbon dioxide, Nature **365**, 589-593

Schlesinger, Melack. 1981. Tellus **33**, 172.

Scott MJ, Jones MN, Woof C, Tipping E. 1998. Concentrations and fluxes of DOC in drainage water from an upland peat system. Environment International **24**(5-6), 537-546.

Searcy JK, Hardison CH. 1960. Double-mass curves. U.S. Geological Survey Water-Supply Paper **1541-B'**

Sharp E, Parsons S, Jefferson B. 2006. The impact of seasonal variation in DOC arising from a moorland catchment on coagulation with iron and aluminium salts. Environmental Pollution **140**, 436-443.

Sillins U, Rothwell RL. 1998. Forest peatland drainage and subsidence affect soil water retention and transport properties in an Alberta peatland. Soil Science of America Journal **62**(4), 1048-1056.

Silvola J, Valijoki J, Aaltonen H. 1985. Effect of drainage and fertilization on soil respiration at three ameliorated peatland soils. Acto Forestalia Fennica **191**, 1-32.

Singer PC. 1999. Humic substances as precursors for potentially harmful disinfection by-products. Water Science and Technology **40**(9), 25-30.

Siren AA, Nilsson M, Shumov DB, Grandberg G, Kovelov AG. 2008. Seasonal changes in the distribution of dissolved methane in the vertical profile of mires of the Zapadnaja Dvina Lowland. Doklady Biological Sciences **361**(2), 348-351

Skiba U, Cresser MS. 1991. Seasonal change in soil atmospheric CO2 concentrations in two upland catchments and associated changes in river water chemistry. Chemical Ecology **7**, 217-225.

Skjelkvale BL, Mannio J, Wilander A, Andersen T. 2001. Recovery from acidification of lakes in Finland, Norway and Sweden 1990-1999. Hydrology and Earth System Science **5**, 327-338.

SNH. 2006. Land cover change in Scotland. Retrieved 12 December 2007 from http://www.snh.org.uk/publications/on-line/education/advances5/4-land-cover.asp.

Stewart AJA, Lance AN. 1983. Moor drainage- a review of impacts on land-use. Journal of Environmental Management **17**(1), 81-99.

Stewart AJA, Lance AN. 1991. Effects of moor drainage on the hydrology and vegetation of northern Pennine blanket bog. Journal of Applied Ecology **28**(3), 1105-1117

Stoddard JL, Karl JS, Devinev FA, Dewalle DR, Driscoll CT, Herlihy AT, Kellogg JH, Murdoc PS, Webb JR, Webster KE. 2003. Response of surface water chemistry to the Clean Air Act Amendments of 1990. Report EPA 620/R-03/001. United States Environmental Protection Agency, North Carolina.

Stumm W, Morgan JJ. 1981. Aquatic Chemistry 2nd edition, Wiley, New York.

Tipping E, Woof C, Rigg E, Harrison AF, Ineson P, Taylor K, Benham D, Poskitt J, Rowland AP, Bol R, Harkness DD. 1999. Climatic influences on the leeching of dissolved organic matter from upland UK moorland soils, investigated by a field manipulation experiment. Environment International **25**(1), 83-95.

Tranvik LJ, Jansson M. 2002. Climate change-Terrestrial export or organic carbon. Nature **415** (6874), 861-862.

Thurman EM. 1985. Organic Geochmistry of Natural Waters. Nijhoff/Junk, Dordrect.

Tuittila ES, Komulainen VM, Vasander H, Nykanen H, Martikainen PJ, Laine J. 2000. Methane dynamics of a restored cut-away peatland. Global Change Biology **6**(5), 569-581.

Turner N. 1757. An essay on draining and improving peat bogs: In which their nature and properties are fully considered. London, Baldwin and Pew.

Tylie F. Smith K. 2001. Degradation of Organic Matter. Wiley New York.

Urban N, Bayley SE, Eisenreich SJ. 1989. Export of dissolved organic carbon and acidity from peatlands. Water Resources Research **25**(7), 1619-1628.

Van Huissteden J, Van den Bos R, Alvarez IM. 2006. Modelling the effect of water table management on CO2 and CH4 fluxes from peat soils. Netherlands Journal of Geosciences- Geologie en mijnbouw **85**, 3-18.

Vassander H, Tuittila ES, Lode E, Lundin L, Ilomets M, Sallantaus T, Heikkila R, Pitkanen ML, Laine J. 2003. Status and restoration of peatlans in northern Europe. Wetlands Ecology and Management **11**, 61-63.

Vaughan GM, Corballis MC. 1969. Beyond tests of significance: estimating strength of effects in selected ANOVA designs. Psychological Bulletin **72**, 204–223.

Velz CJ. 1984. Applied stream sanitation. 2nd edition. John Wiley and Sons, New York.

Verhoff FH, Yaksich SM. 1982. Storm sediment concentrations as affected by land-use, hydrology and weather. Journal of Environmental Quality **11**(1), 72-78.

Waddington JM, Price J. 2000. Effect of peatland drainage, harvesting and restration on atmospheric water and carbon exchange. Physical Geography **21**, 433-451.

Waddington, J.M., Tóth, K., Bourbonniere, R., 2008. Dissolved organic carbon export from a cutover and restored peatland. Hydrological Processes **22**, 2215–2224.

Waiser MJ, Robarts, RD. 2004. Photodegradation of DOC in a shallow prairie wetland: evidence from seasonal changes in DOC optical properties and chemical characteristics. Biogeochemistry **69,** 263–284

Wallage ZE, Holden J, McDonald AT. 2006. Drain blocking: An effective treatment for reducing dissolved organic carbon loss and water discolouration in a drained peatland. Science of the Total Environment **367,** 811-821.

Watson A, Ohare PJ. 1979. Red grouse populations on experimentally treated and untreated Irish bog. Journal of Applied Ecology **16**(2), 433-452.

Watts CD, Naden PS, Machell J, Banks J. 2001. Long term variation in water colour from Yorkshire catchments. Science of the Total Environment **278**(1–3), 57–72.

Webb BW, Phillips JM, Walling DE. 2000. A new approach to deriving "best-estimate" chemical fluxes for rivers draining the LOIS study area. Science of the Total Environment **251-252**, 45-54.

Wilson L, Wilson J, Holden J, Johnstone I, Armstrong A, Morris M. 2010. Recovery of water tables in Welsh blanket bog after drain blocking: Discharge rates, time scales and the influence of local conditions. Journal of Hydrology **391**, 377-386.

Wilson L, Wilson J, Holden J, Johnstone I, Armstrong A, Morris M. 2011. Ditch blocking, water chemistry and organic carbon flux: Evidence that blanket bog restoration reduces erosion and fluvial carbon losses, Science of the Total Environment **409**, 2010-2018

Wright JP. 2003. Water quality in estuarine impoundments. PhD thesis, University of Durham.

Worrall F, Reed M, Warburton J, Burt T. 2003. Carbon budget for a British upland peat catchment. The Science of the Total Environment **312**, 133-146.

Worrall F, Burt TP, Shedden R. 2003a. Long term records of riverine dissolved organic matter. Biochemistry **64**(2) 165-178.

Worrall F, Burt TP, Adamson J. 2003b. Controls on the chemistry of runoff from an upland peat catchment. Hydrological Processes **17**(10), 2063-2083.

Worrall F, Burt T. 2004. Time series analysis of long-term river dissolved organic carbon records. Hydrological Processes **18**, 893-911.

Worrall, F., Burt, T., 2005. Predicting the future DOC flux from upland peat catchments. Journal of Hydrology **300**, 126–139.

Worrall F, Burt TP, Adamson J. 2005. Fluxes of dissolved carbon dioxide and inorganic carbon from upland peat catchments: implications for soil respiration. Biogeochemistry **73**(3), 515-539

Worrall F, Burt TP, Adamson J. 2006. Long term changes in hydrological pathways in an upland peat catchment- recovery from severe drought? Journal of Hydrology **321**, 5-20.

Worrall, F., Burt, T.P., Adamson, J., 2006. The rate of and controls upon DOC loss in a peat catchment. Journal of Hydrology **321**, 311–325.

Worrall F, Armstrong A, Adamson JK. 2007. The effects of burning and sheep-grazing on water table depth and soil water quality in a upland peat. Journal of Hydrology **339**, 1-14.

Worrall F, Gibson HS, Burt TP. 2007. Modelling the impact of drainage and drain-blocking on dissolved organic carbon release from peatlands. Journal of Hydrology **338**, 15– 27

Worrall F, Armstrong A, Holden J. 2007a. Short term impact of peat drain blocking on water colour, dissolved organic carbon concentration and water table depth. Journal of Hydrology **337**, 315-325.

Worrall F, Guilbert T, Besien T. 2007b. The flux of carbon from rivers: the case for flux from England and Wales. Biogeochemistry **86,** 63-75.

Worrall F, Gibson HS, Burt TP. 2008. Production vs solubility in controlling runoff of DOC from peat soils- The use of an event analysis. Journal of Hydrology **358**, 84-95.

Worrall F, Evans MG, Bonn A, Reed MS, Chapman D, Holden J. 2009. Can carbon offsetting pay for upland ecological restoration? Science of the Total Environment **408,** 26–36

Worrall F, Rowson J, Dixon S. In review. Effects of Managed Burning in comparison to vegetation cutting upon dissolved organic carbon concentrations in peat soils. Hydrological Processes.

Yallop AR, White SM, Clutterbuck B. 2008. Evidence for a mechanism driving recent observed trends in dissolved organic carbon release from upland peat soils. Applied Biology **85**, 127–32.

Yallop AR, Clutterbuck B. 2009. Land management as a factor controlling dissolved organic carbon release from upland peat soils. Science of the Total Environment **407**(12), 3803-3813

Young JC, McDermott GN and Jenkins D. 1981. Alterations in the BOD procedure for the 15th edition of standard methods for the examination of water and wastewater. Journal of the Water Pollution Control Federation **53**, 1253.

8. Appendix

8.1 Electronic appendix

The attached disk contains all data used within this thesis.

This includes:

- DOC concentration (chapter 2)
- Flow measurements (chapter 2 and 4)
- BOD (chapter 3)
- Photo-degradation data (chapter 3)
- Acidity and alkalinity calculation (chapter 3)
- Water table data (chapter 4)
- Rainfall record (chapter 4)
- Event analysis (chapter 4)
- Chemical tracers (chapter 5)

8.2 Appendix 2

The following are all the monthly DOC export values for the sites studied. All Units are in tC km^{-2} month^{-1} or tC km^{-2} year^{-1}.

	Cronkley Control			**Cronkley Experimental**		
	CR1	CR2	CR3	CR4	CR5	CR6
Aug-07	10.873	17.937	-	-	-	-
Sept-07	7.868	8.198	9.763	-	-	-
Oct-07	8.732	8.836	9.623	-	-	-
Nov-07	8.172	8.963	10.733	-	-	-
Dec-07	6.962	6.145	7.542	8.762	7.856	6.753
Jan- 08	9.241	8.975	10.538	8.352	9.787	7.242
Feb-08	7.256	7.977	7.866	5.237	6.388	6.253
Mar-08	6.234	6.867	5.098	4.247	5.978	5.453
Apr-08	8.753	7.167	6.242	4.753	5.352	4.980
May-08	3.177	3.456	2.867	1.532	2.542	1.979
Jun-08	2.432	3.678	2.568	1.042	1.544	1.089
Jul-08	3.349	2.965	2.147	1.001	1.252	0.935
Aug-08	3.978	3.867	3.765	1.975	1.419	1.235
Sept-08	9.868	8.967	11.543	9.453	10.332	8.978
Oct-08	9.679	10.177	10.244	9.532	10.912	8.148
Nov-08	8.278	7.979	10.435	8.235	9.322	7.988
Dec-08	6.299	5.901	7.133	6.213	7.879	6.979
Jan-09	6.984	7.753	8.352	7.423	7.185	6.976
Feb-09	7.284	8.009	7.573	6.002	6.974	6.786
Mar-09	7.398	7.148	7.274	5.583	7.353	5.354
Apr-09	7.653	6.214	7.314	4.184	4.872	3.234
May-09	3.184	3.075	3.983	1.131	1.423	1.234
Jun-09	1.897	1.131	1.984	1.004	1.243	0.943
Jul-09	2.492	1.932	2.873	1.199	0.942	0.842
Aug-09	2.143	2.314	2.852	1.009	1.124	0.931
Sept-09	8.327	8.242	9.353	9.424	9.991	8.763
Oct-09	8.293	8.193	9.193	9.472	10.573	8.624
Nov-09	9.472	9.659	12.144	7.864	8.015	7.010
Dec-09	6.972	7.987	7.182	5.914	6.380	6.002
Jan-10	1.525	3.523	2.420	2.984	4.173	3.971
Feb-10	-	-	-	-	-	-
Mar-10	4.242	3.997	4.615	4.086	4.523	3.862
Apr-10	5.243	4.893	5.521	5.833	5.105	4.777
Total						
2008	**78.540**	**77.972**	**80.451**	**61.577**	**72.712**	**61.266**
2009	**72.106**	**71.651**	**80.074**	**60.205**	**66.075**	**56.701**

Table 8.1 Monthly DOC export values for Cronkley Fell. All Units are in tC km^{-2} *month*$^{-1}$ *or tC km*$^{-2}$ *year*$^{-1}$

	Wemmergill		**Atkinson Moss**
	Experimental	Control	
Aug-07	-	-	9.863
Sept-07	-	-	7.863
Oct-07	-	-	4.867
Nov-07	-	-	5.556
Dec-07	-	-	4.876
Jan- 08	3.879	6.234	2.246
Feb-08	6.235	7.313	1.673
Mar-08	8.766	9.234	1.973
Apr-08	8.242	7.242	0.956
May-08	1.333	3.243	0.524
Jun-08	2.435	2.532	0.947
Jul-08	1.435	1.533	0.944
Aug-08	5.254	2.442	1.523
Sept-08	6.342	6.214	4.268
Oct-08	4.242	7.243	3.897
Nov-08	4.255	5.230	3.756
Dec-08	4.235	5.414	2.133
Jan-09	4.243	5.982	3.117
Feb-09	6.946	6.973	3.534
Mar-09	7.254	7.354	2.756
Apr-09	6.352	6.252	1.928
May-09	2.498	2.642	1.042
Jun-09	2.597	3.254	0.728
Jul-09	1.475	1.943	1.067
Aug-09	4.868	4.876	1.687
Sept-09	5.874	6.864	6.274
Oct-09	6.629	7.001	7.108
Nov-09	4.002	5.963	2.924
Dec-09	4.102	5.991	1.931
Jan-10	-	-	-
Feb-10	3.422	2.653	-
Mar-10	4.763	3.853	-
Apr-10	3.531	4.052	2.017
Total			
2008	**56.65**	**63.87**	**24.84**
2009	**56.83**	**65.09**	**34.09**

Table 8.2 Monthly DOC export values for Wemmergill and Atkinson Moss. All Units are in tC km^{-2} *month*$^{-1}$ *or tC km*$^{-2}$ *year*$^{-1}$