Dissolved organic carbon (DOC) management in peatlands

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Abstract

Peatlands are serving as one of the most important terrestrial carbon stores in the United Kingdom and globally. In the UK, the current trend of peatlands turning from carbon sinks to carbon sources is widely observed and reported. As numerous factors may affect the carbon cycle of peatlands, including climate, land management, hydrology and vegetation, dissolved organic carbon (DOC) was commonly used as an indicator of peatland carbon changes. Besides the function as an indicator of carbon turnover in peatland, increasing DOC in the stream water also raises concern in water companies as the removal of DOC from water represents a major cost of water treatment.

This thesis investigates the impacts of land management such as drain blocking and revegetation on stream DOC changes. By building a pilot column study, this thesis also assessed the potential of bank filtration serving as DOC treatment in UK.

Results of drain blocking shows the management was a significant impact on the DOC changes. However, later investigation of peak flow events indicates such positive impacts from drain blocking were minor in terms of high peak flow events. Since the majority of DOC export occurred during such peak flow events, drain blocking were found not as an efficient management of DOC changes. The field study of revegetation observed minor effects of revegetation on stream DOC. The results of column bank filtration indicate low DOC removal rate under the current stream DOC level in UK. The bank filtration may efficient remove DOC when higher DOC input applied. However, it is not suitable for UK peatland under current DOC export.

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, material from the work of others has been acknowledged.

Signed:

Date:

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Chapter 1 Introduction

The aim of this chapter is to discuss the widely observed increases in stream water dissolved organic carbon (DOC) concentration from northern peat lands and attempts to reduce these DOC releases from peatland. A variety of possible causative factors will be discussed, including the effect of burning, grazing, drain blocking; and the influence of severe drought.

1.1 DOC problem

Peatlands cover about 4.16 million km^2 worldwide, with 80% of the peatland area situated in temperate-cold climates in the northern hemisphere (Holden et al, 2011), and typically as the UK, the peat bogs are seen as the largest carbon reserve (Cannell et al, 1993). As part of the Kyoto protocol (UNFCCC, 1992), developed countries are committed to reducing greenhouse gas emissions to 5% below their 1990 level by 2012, which highlighted the need of control of carbon release from peatland. Also, according to the demands of the United Nations Framework Convention on Climate Change (UNFCCC, 2001), countries would meet their target by accounting for the carbon sequestration on grazing land since 1990. Therefore, the peatland in UK, which are mostly grazing land, are vital to meet the policy requirements (Worrall et al, 2006). In UK, the peatland are currently still seen as the sink for atmosphere carbon (Worrall et al., 2003), however, as it is largely managed for forestry and recreational shooting uses is as also receive influence from atmospheric deposition and tourist pressure, the UK peatland soil may be fragile to damage (Clay et al, 2010). There is increasing evidence of increasing carbon turnover, which indicates that peatlands are in the process of switching from a sink to a source of carbon. For instance, Freeman et al.(2001)

have shown increase in DOC concentration of 65% for 11 UK stream and lake catchments over the last 12 years. The majority of carbon losses in UK peatland are as aquatic fluxes of carbon (Dinsmore et al., 2010). There are numerous pathways for releasing the carbon from peatlands which are related to changes in the depth to the water table, for instance increased decomposition following the increased aerobic condition as the water table depths increase (Christensen et al., 1998); and nitrogen supply changes may cause the shifts in carbon storage (Updegraff et al., 1995). Among these pathways of carbon release is the flux of DOC, and therefore, the control of DOC release is important in controlling carbon balance in peatlands (Figure 1.1).

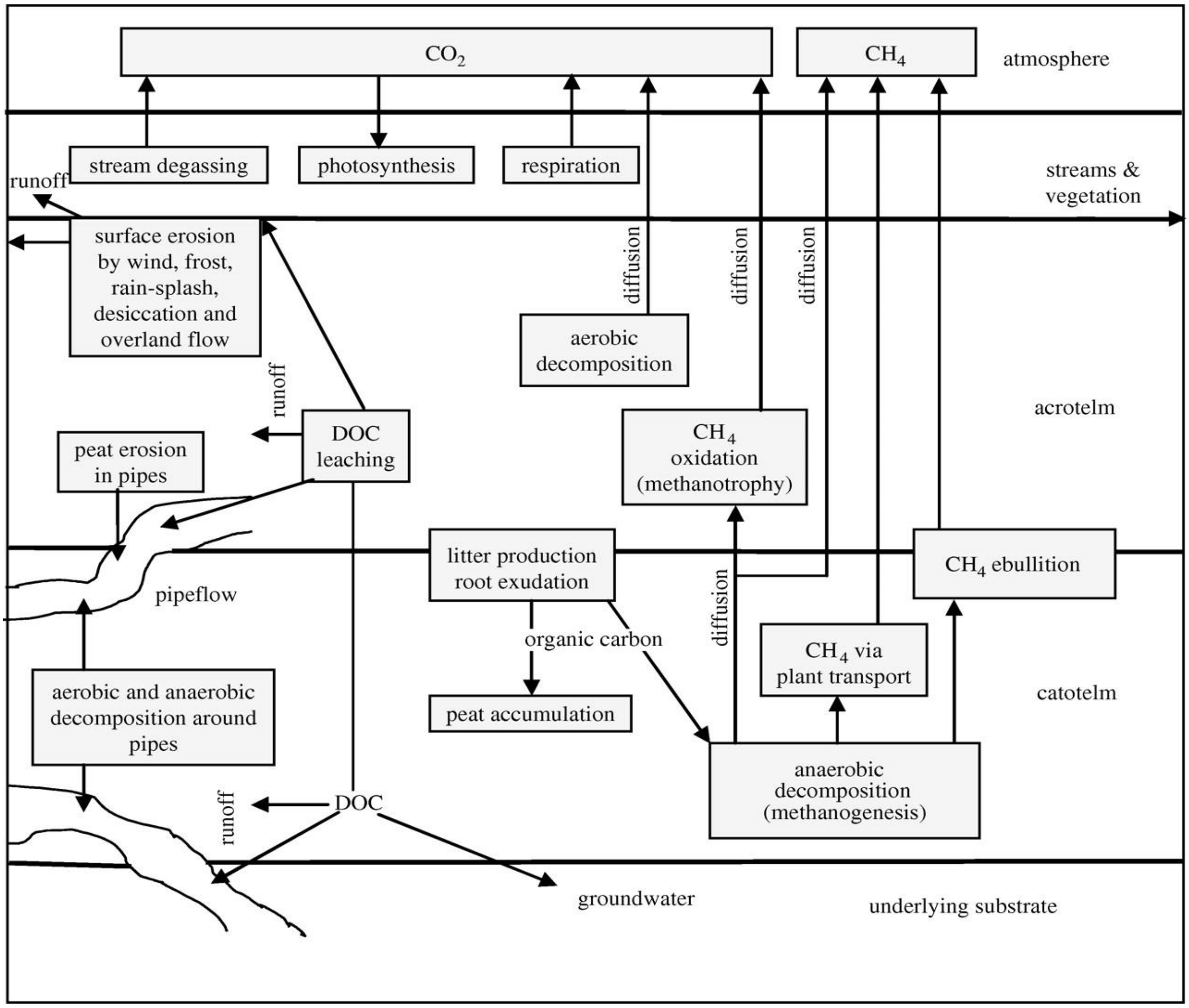

Figure 1.1: Components of the carbon cycle in peat. (Holden at al., 2005)

Also, among the aquatic components, dissolved organic carbon (DOC) is generally considered as the largest contributor to carbon loss (Limpens et al, 2008). The increasing release of DOC have also been observed by a range of studies observed in North America (Discoll et al., 2003); central Europe (Hejzar et al., 2003). For UK, Worrall et al. (2004) have shown that among 198 catchments studied, 77% of them showed a significant increase of DOC concentration on the time scale between 9 to 42 years (Figure1.2).

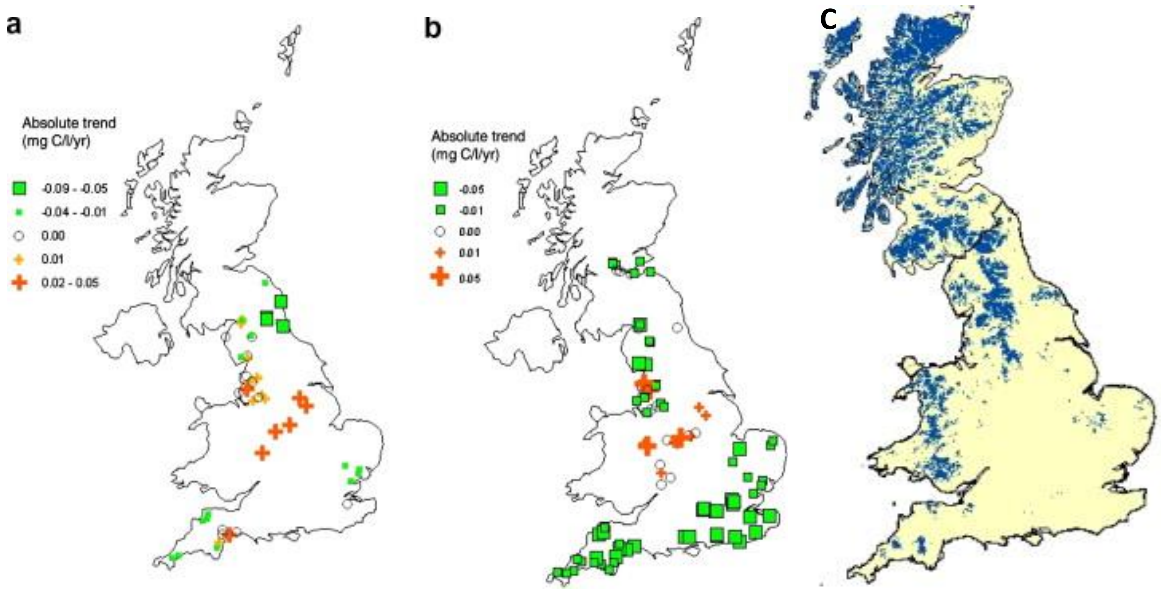

Figure 1.2 (a) The DOC loss trend in the UK from 1997 to 1986. (b) The DOC loss trend in the UK from 1993 to 2002. (c) The distribution of peat soils based on Host classification (Worrall and Burt, 2008).

The concern over DOC release is not just a concern over soil carbon storage. The removal of DOC from water represents a major cost of water treatment known as water colour, which is often used as an indicator of DOC release. Unsuccessful removal of water colour may cause aesthetic problems for drinking water supply, interfere with disinfection processes, and breech environmental standards (such as EU Water Framework Directive, 2000/60/EC). Increased requirement for the removal of water colour would increase the cost of treatment for water (Wilson et al., 2011). The coagulant can flocculate the DOC and so remove the water colour, however treatability could be expected to change with changes in concentration and composition as a result of the enzyme-latch process (Freeman et al., 2001). The enzyme-latch process results in increased release of phenolic compounds that are part of the DOC and phenolic compounds are strongly absorptive of light, and therefore the DOC release would become more coloured per unit of DOC (Worrall and Burt 2010). The enhanced level of decomposition after restoration can also leads to the formation of highly coloured, bio-resistant humic organic material, which may be maintain a highly resistant under land management or climate change (Wallage and Holden, 2010). Therefore, the removal of water colour is strongly related to the treatment of increasing DOC.

1.2. Long-term records of DOC

Long-term records of DOC concentration in surface waters and lakes exist for many locations in the UK. The observation of DOC is not always directly measured, instead, water colour is often used as a proxy for DOC concentration. In a study of three catchments in North England, a significant increase in water colour was observed in two catchments over a period of 39 years, through no increase was observed in the third catchment, and the inter annual control on carbon releasing in response to droughts was suggested as the cause (Worrall et al., 2003). The distribution of the daily values of DOC concentration and water colour may be the cause of the differences between three catchments. In other words, the accuracy of the measuring methodology in DOC- colour relation, which cause the observed differences. The difference might be caused by the different land use such as the different drainage in different catchments. What's more, when coupled with the severe drought, the enzymatic latch mechanism might be triggered, as Freeman et al. (1999) implied. In his mechanism the falling of the water table would enhance the phenyl oxidase and restricted hydrolase enzymes which lead to the destruction of the phenolic compounds and continuing decomposition even after the restoration of water table, which contributes to the carbon release (Holden, Worrall, 2003). As cited before, the phenolic compounds then would make DOC release more coloured (Worrall et al.,2010). This change is apparently related to the change of the DOC composition and therefore could be easily tested by the change in the level of the water colour. What's more, an alternative mechanism (Clark et al., 2005) also related the DOC increases to the severe drought, in which the effects lies on the oxidation of the sulphate minerals present in peat to sulphate which suppress the DOC solubility and then recovery from drought causes increased DOC release. This process is also an explanation for the observed correlation between declines in atmospheric deposition and increased DOC release from peat bogs. Thus, the changes in the hydrophobic fraction would become more coloured, which also indicted the changes of DOC composition. Furthermore, as Lumsdon et al. (2005) indicated, even changes in air temperature would lead to the changes in DOC composition. However, the expected compositional step changes in DOC records were not observed and the records of the DOC compositional changes are rare (Worrall and Burt, 2010). Besides, no correlation between river discharge, pH, alkalinity, rainfall and increasing colour trend were shown in the study (Worrall et al., 2010), but summer temperature trends were indicated as a possible trigger for the observed DOC concentration trend. The distribution of daily values also suggested a change in sources in colour over the trend. From the study of Worrall et al. (2010), it is clear that the changes in the water colour were not caused by the change of DOC flow but may be an effect of long-term variation of the composition of DOC. Thus this limitation should be noted when using water colour as an indicator of DOC.

When extended to national scale, Worrall et al. (2004) considered 198 sites varying in duration from 8 to 42 years, going back as far as 1961, and showed a consistent DOC increase through trends may have been hidden by increasing discharges over the same period. Possible reasons for the observed trends were increasing temperature and the increased frequency of severe drought. The effect would be accentuated when combined with land use change and eutrophic ratio (The ratios of different forms of nitrogen to phosphorus). Long term DOC observation indicated that upland catchments would be a net source of carbon during periods of drought. This result suggested a single upland peat catchments over a ten year period would become a net source, instead of a net sink (Worrall et al., 2007).

In summary, the DOC and water colour are increasing and there are several hypothesis for the possible changes, as cited earlier with climate change caused rising temperature and the frequency of severe droughts probably the main driver of this trend.

1.3. Alternative explanation of increasing DOC

With the concern of increasing DOC release from the catchment, there are several possible hypotheses to explain the observations, these include: increasing air temperature (Freeman et al., 2003); change in land management (Worrall et al., 2003); changes in pH (Kung and Frink, 1983); change in the nature of the flow (Tranvik and Jansson, 2002); eutrophication (Harriman et al. , 1998).

Over the period of observed records, the temperature of UK has been rising (Worrall et al., 2010). It is proposed that the increasing temperature has two effects on release of DOC: 1) directly or indirectly faster decomposition reactions; 2) increased DOC solubility; 3) increased drawdown of water tables which increases rates of the process of oxidation. However, Tipping et al.,(1999) proposed, that instead of increases in temperature, it is the combination of warming and drying cycle that leads to increases in DOC release. Further, the observed effect is built on the 1 K rise in air temperature compared against an almost 100% increase over the same period in the DOC concentration. Thus, the temperature changes appear too small, unless it combined with other trigger mechanisms.

The influence of acidity upon DOC production was raised by Krug and Frink (1983). However, the evidence from later fieldwork was unequivocal. Both Holden et al. (1990) and Wright (1989) indicated that the effects of acidity are small and non-existent. Further, the assumed linear relationship between DOC increase and pH increase were not found (Worrall et al., 2003). Although the changes in pH may result in the changes in DOC composition, it still was not possible to see it as a main factor of DOC concentration change.

Changes in the nature of flow could cause a rise in DOC concentration. It could be caused by the increasing headwater contribution to flow in large catchments, or increased storm runoff, without changes in overall discharge, which will increase DOC bypass through both subsoil horizons and surface, organic-rich peat (Tranvik and Jansson, 2002). However, this later study did not provide evidence to support the hypothesis.

In UK upland streams, evidence has been found to support that eutrophication from N-deposition may be the main factor controlling the changes releasing DOC (Cole et al., 2002). This reaction is mainly driven by the increase activity of the enchytraeidae worm which influenced by the temperature change, would increase microbial activity and therefore enhance the DOC release. However, the scale of this effect is too small compared to the large observed increase in DOC concentration. Conversely, Harriman et al. (1998) showed that it is the DOC increase that is causing the eutrophication and not vice versa.

It seems that correlation between any of these factors and increasing DOC concentrations was equivocal and none of these possibilities, when considered as single factors, could be considered as the main explanation. An alternative hypothesis is the action of drought as a possible driver in the DOC release of UK peatland (Worrall and Burt, 2005).

The mechanism by which severe drought could lead to an increase in DOC losses from peat have four possible hypothesis 1) The enzyme - latch mechanism (Freeman et al., 2001); 2) Creation of new pathways; 3) Dried peat causing water exclusion from parts of the peat matrix; 4) crusting of surface preventing infiltration (Worrall et al., 2006). According to the observations by Edwards and Cresser (1987) and Worrall et al., (2002) it is possible that not only the hydrological changes results in DOC increase but also the physical effects of drought will lead to the DOC increase. To test these hypotheses, Worrall et al (2005) used single and multiple tracers from long-term records of stream chemistry. As the hypothesises predicted , there would be expected to observed two consequences:

1) a lower conductivity in streams caused by a decrease in residence time or interaction between mobile and immobile water; and
2) an increasing influence upon the soil water chemistry in the catotelm, thus the deep soil water may become more rain water like.

However, none of these consequences were observed. By contrast, the observed changes in conductivity suggested that the evaporation may increase the residence time rather than decrease it (Worrall et al., 2006). Furthermore, long periods of influence of drought were not observed, except for an offset between drought and maximum stream water concentrations of Fe, DOC, Al (Worrall et al., 2006). These observations then suggested that the continuing drought effect were due to consequences for DOC via enzyme-latch production and hydrophobic effects rather than the assumed physical changes in flow path (Worrall et al., 2006). The study also indicated that the increased DOC post drought occurred in the soil matrix, which did not have its full effect until the next major water table drawdown in the following summer. The peatlands would become ever increasing sources of DOC if the general re-wet process was not finished before the next severe drought occurred, i.e. the drought return period is too short to let the peat catchment recover. In order to evaluate this process, Worrall et al. (2005) built a first- decay process concerning the enzyme-latch process and recovery from this biogeochemical effect. Worrall et al. (2006) concluded that the study site is close to a balance point where the effect of drought would continue even after that the return period of the drought, which means that a new position of equilibrium is never achieved. In other words, the peat catchments in summer are hydrologically independent of the winters because of the limitation arising from severe drought. Therefore, the balance between the return period of severe drought and the time constant of the recovery from drought might be the main control upon the biogeochemical consequences of drought.

However, the hypothesis that the severe drought caused the DOC increase was challenged by later research. Worrall et al. (2008) compared monthly and annual DOC flux estimates to the total flow, total rainfall, actual evapotranspiration (AET) and average temperature. Most of these comparison show a high degree of collinearity, the best-fit equation between DOC flux and different drivers were then been built on two levels. The test for the drought effect used the residual magnitude after removal of the best-fit equation. If the drought effect did have a further influence upon the DOC flux an increase in the residual should be observed. However, no significant decline was observed, and furthermore, no significant relationship between annual DOC flux and drought effect measurements have been found (Worrall et al., 2008). The earlier evidence cited by Worrall et al. (2005) showed severe drought influenced DOC flux mere can be explained by :1) earlier estimates of enzyme-latch time constant are in fact the cyclicity of the river flow

(Worrall et al., 2008); 2) The CO_2 respiration was limited by the organic matter turnover not the flux of DOC. Worrall et al. (2006) also indicated the present literature of DOC trends might be exaggerated by the relatively short period of the available records. Like other possible hypothesizes, the drought mechanism has not yet proved to be a fully acceptable explanation of rising DOC concentrations. Indeed, there may not be a single hypothesis that covers the whole reason causing the increasing release of carbon from the peatlands. The use of land management is commonly used among UK peatland and therefore could be a main contributor of the DOC release from peatland.

1.4. Land management

Land management in UK peatlands commonly includes grazing, burning and drainage. These management practices would initially cause the fluctuation of the water table and could be coupled with climate change to increase the water colour (Worrall et al., 2003). Further, land management like afforestation and drainage has been reported as widely used in peat land in the UK, the management of afforestation can disturb the water equilibrium, which will lead to carbon release (Worrall et al., 2003). Worrall et al. (2008) examined the flux of the DOC and indicated that the most likely treatment of the control for the DOC releasing is to limit the runoff of the catchments, which, in the case of the UK, might be largely influenced by the variations of water table (Holden et al., 2011)

Normally, the water table depth in intact peatland is close to the surface during most parts of the year and water table fluctuation are generally limited (Holden et al., 2011). However, as cited before, the peatlands in the UK are usually drained in response to some severe drivers, including 1) enhanced agriculture demand in marginal areas of productivity; 2) land for afforestation; 3) the demand for horticulture and energy production; 4) the prevention of the flood risk (Holden et al, 2011). However, results of studies usually fail to find a significant impact due to the draining (Stewart et al., 1991). The failed attempts to find drain impact on DOC changes could be caused by the low saturated hydrological conductivity or the wrong focus on the distance away from drain where the drawdown couldn't be observed (Holden et al., 2003). Also, if the pools are generally receiving influence of the local slope and the hydrological integrity of dams (Armstrong et al., 2009), then the blindness of the spatial and physical dynamics, such as the difference in layer on either side of the drains, may influence the result of the observed fluctuation (Holden et al., 2011).

Drainage of peat could drawdown the water tables, expend the area of oxygen in drained area and thus stimulate DOC production. However, the extension of land management over time would still not fit the observed increase in DOC concentration and therefore Worrall et al. (2003) suggested them to be accentuating factors.

1.4.1. Burning and grazing management

In UK, most upland peat catchments are used for grazing or breeding animals and 40% of English peatlands are under burn management (Worrall et al., 2008, quoted Thomas et al. (2005)). The rotation timescale of burn managements is normally between 7 to 20 years and so the impact of burning would require a long periods of observation (Worrall et al., 2007). Using long-term monitoring sites, Worrall et al. (2007) showed that:

1) both the grazing and regular burning leads to a different water table depth as both management strategies limited the development of vegetation;

2) the burning process controlled the pH and conductivity of soil water; and

3) DOC was largely dominated by date of collection, but soil water concentrations were lower on both burned and grazed areas when compared to unburnt and ungrazed areas.

However, it should be noticed that the results were limited to the behaviour of soil water composition, which cannot directly reflect the composition of runoff from the managed catchment (Worrall, et, al., 2007). Furthermore, the study only considered the end of the burning cycle, and could not compare the changes before, or after a burn. Later research on soil water composition showed that significant difference between burning treatments but only slight differences were found on grazing (Worrall and Adamson, 2008). This is because grazing has less effect on water table depth, compared to the effect of burning and vegetation. On the other hand, the results shows the water table difference between burned and unburned sites may be caused by the vegetation development and evaporation, where unburned area have higher evaporation and vegetation leads to draw in deeper water table with distinct composition. Some studies were focused on finding evidence for soil structural changes. If such a change happened, new flow paths may appeared which may explain changes in the DOC concentration observed by Worrall et al. (2007). The analysis (Clay, 2011) did show there was no interaction between shallow and deep soil water, however the tracer also showed, that upon burning, the soil water composition became more soil-like and less rain-water like. The increasing similar composition in soil water may indicate to the changes in interaction between incoming water and the peat soil, not a creation of the new flow pathways. The result were collected at the end of burning, which may indicated that after the burning changes may consisted long period and may be severer immediately after burning.

The study on the runoff of the stream (Clay, 2009) showed the influencing factors included:

1) The rising water table;

2) The increased rainfall water to the surface caused by the remove of the vegetation (Soto et, al ,1997);

3) Burning increased hydrophobic compounds, decreasing the interaction with soil and facilitated them to surface flow (Debano, 2000);

4) Physicochemical feedback caused by the burning process (Mill and Fey, 2004).

Clay et al. (2009) found no significant burn treatment and DOC concentration interaction, but a low DOC concentration was observed in runoff water related to soil water. The trend indicates that unlike the soil water, the runoff water may receive influence from grazing (Clay et al., 2009). Further in a later study of a ten years prescribed burning, Clay et al., (2015) suggested that with the better understanding of the complete burning cycle, the burning effects on whether the burning would bring about carbon benefits are equivocated. In the same study, Clay et al., (2015) also implied the importance of the changing of revegetation upon the peatland management: although study of *Calluna* – dominated burning avoids the carbon losses by changes in the magnitude of sources, peatland would benefits more by the vegetation change to the more actively peat forming system (Clay et al., 2015).

1.4.2 Drainage management

Besides the grazing and burning, the use of drain blocking as a possible land management to restoration is then widely discussed (Turner et al., 2013). Normally, the restoration practice of the peat catchment is rarely by complete infilling, instead, the drain blocking is achieved by installing dams and providing pools. Holden et al. (2011), have shown that drained sites tend to have less water reaching them from upslope and, therefore, the water table maybe lower on one side of the drain than the other. Hence drain blocking can be claimed to solve this problem by supplying a pool of water that seeps through the hill slope, therefore, drain blocking might be a possible pathway to control the DOC release.

However, the efficiency of drain blocking is doubted by the results of some studies which show a conflicting trend. Daniels et al. (2008) and Holden and Burt (2002) showed the evidence that the raised water table may increase the flashiness which may indicate efficiency of drain blocking. This findings is then challenged by Armstrong et al. (2010) who found a decrease in DOC and discharge upon drain blocking. The two findings are indeed conflicting and require further study for explanation. Possible reasons are listed by Wilson et al. (2011), whom indicated that the conflicting results may have been caused by the variations between the study sites, but these differences also require further investigation.

The study of Holden et al. (2011) showed that the blocked drains appeared to have hydrological functions moving towards the level of intact drains, however, this is varied owing to spatial and physical impacts. In the long term, the dynamics of these restored peatlands are doubted, and even if the hydrological function is restored, the timescale is much longer than anticipated by most restoration programmes (Holden et al., 2011). Wilson et al. (2011) and Tuner et al. (2013) did a study on the DOC concentration trend after the drain blocking; the effects were somehow minimal and limited. Wilson et al. (2011) estimated the DOC concentration for two study sites: an unblocked drain (A) and a post-blocked drain (B). The results showed a decline in DOC concentration after the drain blocking (Wilson et al., 2011), matching the study of Gibson et al. (2009) who also showed that changes in DOC concentration are probably small in magnitude after blocking. The increase of DOC might be because of the sharp decline of flow rate and yield decline after drain blocking (Wilson et al., 2011). On the other hand, Armstrong et al. (2010) showed that a blocked drain had a higher DOC concentration with higher flows than those of unblocked drains. Wilson et al. (2010) indicated the importance of the discharge rates in determining overall organic carbon losses. The hypothesis that water table depth would control the DOC behaviour has been tested by Turner et al. (2013) and results for DOC export showed that the reduction in export was only 9.2% at zero-order drains and 2.2% at first-order drains, i.e. the effect of drain blocking was lost at larger scales. There are potentially several reasons for the small effect of drain blocking. The bypass flow around the blockage was observed to add high DOC concentration to the runoff flows down the drain. The alternative hypothesis was proposed by Freeman et al. (2001), the so-called 'enzyme latch 'mechanism', by which hydrolase enzymes increase the DOC production and this process will not stop right after the restoration of the water table. However, Wilson et al. (2011) has showed a reduction of DOC from deeper peat simultaneous with drain-blocking, but failed to found evidence to support the 'enzyme latch' mechanism. Furthermore, the effect which caused by the change of water table depth observed by Tuner et al. (2013) was only 1 cm. The results of Tuner et al. (2013) also matched the result of the study of Gibson et al. (2009), which showed that the drain blocking did decrease the export of DOC but only achieved by decreasing water yield. What's more, the observed decrease in absorbance and DOC concentration could only explain 1% of variation in their data. Thus, the use of drain blocking to control the DOC release is an equivocal factor and needs further observation.

The changes of hydrological regime associated with drainage management are likely to alter runoff response from peatland (Ballard et al., 2012). The hydrological regime changes of peatland, which cause potential inimical changes of peatland runoff and raises the chances of erosion have been widely discussed (Worrall et al., 2006, Holden et al., 2007). Observations suggest that increased temperature and changes in rainfall patterns could leads to the production of DOC (Worrall et al., 2004, Clark et al., 2007). Unlike the widely discussed drain blocking effects on the DOC export, the drain blocking impact on peak flows has not been conclusively covered by research to date. The concentration of DOC has been associated with discharge and frequently correlated to storm events.(Austnes et al., 2009). Several studies has illustrated the correlation between DOC export and flow path changes in the organic mineral soil (Dawson et al., 2002; Soulsby et al., 2003). The concentration changes of DOC has been associated with the flow path changes where the higher DOC concentration from increased lateral flow through the upper horizon compared to the lower horizon were exported with peak flow in organomineral soil (Worrall et al., 2003). Peat and organic mineral soil differ in terms of profile and hydrological behaviour, and therefore DOC dynamics would also differ in response of the storm events. In peatland, the carbon stored in lower horizon (catotelm) is hydrologically disconnected from the stream (Billett et al., 2006, Clark et al., 2007) where the base flow of the stream is characterised as alkaline poor ground water (Worrall et al., 2002) and hydrologically connected between peat and the mineral soil. When the water table rise during the peak flow event, the upper horizon (acrotelm) flow with DOC rich soil water would raise the stream DOC concentration (Worrall et al., 2002, Clark et al., 2008). Holden et al. (2011) further indicated that DOC export is controlled by either saturated overland flow and macropore flow of peat matrix, or direct rainfall dilution during the peak flow events. The drainage area were correlated with peak flow event water contribution to storm (Pearce et al., 1990; Brown et al., 1999).

1.4.3. Revegetation

The main effects of peat land management e.g. peatland drainage and burning includes changes of water table, hydrology, water quality, sediment flows and vegetation (Bellamy et al., 2012). The peat land restoration in UK is typically carried out by drain blocking in which water table been raised (Turner et al., 2013) and in turn the blocking also encourages the growth of peat formatting plant species (i.e. *Sphagnum*) (Holden et al., 2007; Peacock et al., 2013). Restoration by drain blocking often helps to reestablish the vegetation. The pioneering plant species such as *Sphagnum* often are indicative to the changes of species' associated with improved fluvial carbon balance. In particular the recolonization of such pioneer species are dominant and reestablished faster than the original species that covered peat (Palmer et al., 2001; Robroek et al., 2010). The impact of the revegetation on DOC export is highlighted as Parry et al. (2014) demonstrated that surface roughness may play a more dominant role in terms of peak flow events. The transition from the bare peat to vegetated peat would yield greater storm flow changes in rivers than blocked drains. Thus, the revegetation would initially decrease the overflow and decreases the DOC export. However, other studies (Robroek et al., 2010) indicate although the particulate organic carbon (POC) of runoff water from peat land were recorded as having been stabilized through the revegetation, DOC concentration and vegetation were found to be uncorrelated to each other following the drain blocking (Bellamy et al., 2012; Kopeć et al., 2013; Peacock et al., 2013). Unlike drain blocking, other land management such as burning strongly effected the vegetation and often leads to significant changes in carbon cycle and hydrology (Brown et al., 2015). The vegetation affects soil water balance through growth dynamic, transpiration and interception. The removal of vegetation would elicit the chance of a runoff event and thus introduce more DOC to the stream water (Robroek et al., 2010; Kopeć et al., 2013). Further, vegetation removal with fire can significant alter the energy balance duo to the exposure of more bare peat to solar radiation and therefore leads to the changes of soil thermal regimes and thus leads to changes in carbon cycling, often with simultaneous increased DOC concentration (Kettridge et al., 2012; Brown et al., 2015). The revegetation with improving of self-regulated acrotelm by retaining high moisture level beneath the plant canopies would lead to the substantially increased stability of the DOC production from the peat (Ballard et al., 2011). Most studies are focused on the vegetation communities' changes following peatland restoration (Brown et al., 2015); the relationship between vegetation and ground water table (Kopeć et al., 2013). There is little in the literature about revegetation impacts on DOC export followed by burning apart from Qassim et al. (2014). The study (Qassim et al., 2014) looked through 5 years field study of the burned and revegetated site in comparison of both a bare peat control and vegetated none –restored control. The result of this revegetation study found a significant import of DOC in the soil pore water of revegetated site in comparison to the bare peat and vegetated site and no significant difference between soil pore water DOC concentration and runoff DOC contortion. Qassim et al. (2014) also highlighted the possible drawdown of DOC export in the runoff with the water table restoration alongside the vegetation. Therefore, further study of revegetation effects on DOC runoff should be considered.

1.5 Bank filtration

Besides the possible land managements listed above for carbon release, other possible hypotheses for prevention of DOC release might be considered. Bank filtration, for instance, is widely used as a efficient water treatment both in Europe and United States (Grunheid et al., 2005). In this process, the primary aim is to remove the pathogenic microbes from the raw water, but also biodegradation processes would initially remove turbidity and DOC (Grunheid et al., 2005). Therefore, bank filtration could be used as a possible management to remove DOC. However, it should be noted that there are big difference between how Europe and North American have reportedly used bank filtration which initially might arise because of the designed retention time. In Europe, the retention times are mostly designed for several weeks or even months according to the straight demand for the drinking water whereas, in North America the retention time is only ranging from several hours to days, at most a few weeks. As the DOC removal is mostly based on the biodegradation process of bank filtration, the redox condition is then highlighted as its control and the need for changing retention time (Grunheid et al., 2005). This is also supported by the research of the Kim et al. (1997) who indicated no significant differences between absorbed DOC in winter and summer and the percentage of biodegradable DOC was higher in the winter than in summer probably due to active biodegradation in the reservoir in summer. Furthermore, zonation was not effective to change the molecular weight of organic substance, but could enhance biodegradability of DOC and reduce absorbance in UV 260nm. It should be noted that even through the bank filtration could decrease the DOC level of stream water, there is a potential danger to introduce other contaminated compounds to the water sample, such as the increasing the dissolved iron by the degradation through aquifers (Kim et al., 1997). Either natural or induced through the river bed by pumping from a system of connected lateral or vertical wells, riverbed clogging's beneficial effect on promoting the biogeochemical degradation of contaminants and its disadvantage on the reducing the hydrological conductivity of the infiltration zone (Hiscock and Grischek, 2002) were noticed. Mostly, these pump locations could be set near to the riparian zone near the drains (Fiebig et al., 1990). The possible effects of the riparian zone on the DOC releasing is then discussed, with again some studies showing that the riparian zone can contribute substantial amounts of DOC to a stream ecosystem, and that the stream bed must be a key area of chemical reactivity where much of this material is initially processed. As the delivery of DOC to the stream bed will depends on the hydrology of the riparian zone, knowledge of this is an essential prerequisite to modelling the transfer of organic material from a catchment to a stream. It is indeed unclear how the effects of the hydrology process would also potentially 1) increase the DOC instead of the suspended 2) sometimes decreasing when building bank filtration on riparian zone and pump water from stream through aquifer to dip wells. Thus, it is necessary to undertake further study of the bank filtration of the riparian zone.

1.6 Aim and object

This introduction chapter has illustrated the importance of the management of DOC upon the UK upland peat with is impacts on both the carbon cycle and water treatment. A series of heated researches has been interested in the effect of land management upon the peatland (Gibson et al., 2010; Worrall et al., 2014), especially the impact land management may have on the DOC. Studies of the burning and grazing of peat land carbon management (Worrall et al., 2008; Clay et al., 2015) found both the burning and grazing were equivocal on the effects which benefits the carbon sink. Therefore, this thesis will focus on the work of DOC management through land management such as drain blocking, revegetation and a pilot study of potential use of bank filtration as tools of such management. Despite the effects such as those described by Turner et al. (2013), which previously contributed on the drain blocking effects on DOC management, the impacts of peak flow events on the such management have rarely been discussed. This present work also included a chapter of peak flow events upon drain blocking effects in which would hopefully enhance a better understanding of the drain blocking as a management of DOC in upland peat.

This can be broken down to series of specific objectives:

1) Measurement of the DOC concentration and budget on a series of nested and blocked catchments. Chapter 2 will be dedicated on such aim by assessing a five year long field observation on drain blocking in Northern England. By comparing the DOC concentration and export from both blocked and unblocked catchments in the study site over the periods before and after the blocking applied to site, decreased DOC exports and concentrations would be expected duo to blocking.

2) Access the blocking effects upon the peak flow events in upland peat. Following the findings and discussion on drain blocking in chapter 2, Chapter 3 will be focused on the drain blocking impacts on DOC during the peak flow events. If the drain blocking was proved to be an efficient practice of controlling the DOC releasing from peat soil during the study period in Chapter 2, then drain blocking would be also expected to be an efficient practice during the peak flow events during study periods. It is crucial to assess the efficiency of drain blocking during peak flow events, as the most DOC exports from soil to water were occurred during peak flow events.

3) Assess the impact of revegetation on DOC changes in upland peat streams. As a common management in Northern England peat, cool burning was widely applied (Clay et al., 2009). Chapter 4 will assess how revegetation affects DOC release to stream runoff after cool burning by comparing a revegetated catchment and a bare catchment site. Revegetated catchment compare to bare catchment would expected a much more stable water table and thus may lead to an also more stable and lower DOC export over the study periods.

4) Assess bank filtration as an alternative approach to the management of high DOC concentrations. A pilot study was performed on the side of the major field observations to assess alternative management to drawdown runoff DOC in chapter 5. The assessed management is bank filtration, where was successfully applied in Germany as water treatment and proved to decrease the runoff DOC (Grünheid et al., 2005). By conducting a column study to mimic the filtration process using river bank soils from river wear, filtrated water DOC would use to compare with the runoff water DOC to assess whether the practice is suitable for river wear or not.

Chapter 2 Drain blocking

2.1. Introduction

This study was designed to evaluate the potential positive influence of drain blocking on dissolved organic carbon (DOC) releasing from peat. There are several reasons for concern over DOC with respect to water quality that was discussed in detail in chapter 1. These can be summarised as:

1) Peatlands in the UK could be changing from a carbon reservoir to carbon sources (Freeman et al., 2001), and an important component of the carbon release in UK is via aquatic flux (Dinsmore et al., 2010). The aquatic flux of carbon from peat soils is commonly related to changes in the depth to the water table. Dissolved organic carbon (DOC) flux is one of the most important pathways of aquatic carbon release. At the same time, DOC is also generally considered to be the largest contributor to aquatic carbon among the aquatic components (Limpens et al., 2008).

2) The removal of DOC from water is a major water treatment issue. Unsuccessful removal of DOC may cause aesthetic problems in drinking water supply, which is a key part of the disinfection process (Wilson et al., 2011), and breech environmental standards (such as EU Water Framework Directive, 2000/60/EC).

There are several possible hypothesises to explain the observed increase in DOC release from peat soils that have been outlined previously (Chapter 1). Among all of the explanations it is clear that water table fluctuation is seen as an important factor, which highlighted the importance of managing a stable water table in control of DOC releasing from peatland (Worrall et al., 2008; Holden et al., 2011).Several common land management practices could influence DOC release from peat bogs, these include: grazing, burning and drainage. These management practises would initially cause the fluctuation of the water table which could couple with climate change to increase the release of DOC. Normally, the water table depth in intact peatland is close to the surface during most parts of the year and water table fluctuations are generally limited (Holden et al., 2011). However, the peatlands of the UK are usually drained in response to resource demand, including 1) enhanced agriculture demand in marginal areas of productivity; 2) afforestation; 3) horticulture and energy production; 4) prevention of flood risk (Holden et al., 2011). Therefore, the drawdown of the water table in drained blanket peat was observed throughout the UK (Holden et al., 2011). However the observed results usually fail to find significant impact between the drain and drawing down of the water table. (Stewart et al., 1991). As listed in chapter 1, the failure of finding impacts between DOC and water table might be caused by the site difference (Holden et al., 2003) or slope effects of the study site (Armstrong et al., 2009).

In case of providing a stable water table, which initially may control the DOC release, the uses of drain blocking as a possible land management for peatland restoration is widely discussed (Turner et al., 2013). Normally, the restoration practice is rarely achieved by completing infilling, instead, the drain blocking is achieved by installing dams and providing pools. Holden et al. (2011), have shown that drained sites tend to have less water reaching them from upslope and, therefore, the water table maybe lower on one side of the drain than the other. Hence, the drain blocking might solve this problem by supplying a pool of water that seeps through the hill slope. Therefore, drain blocking alters depth to water table and could alter flow paths through the peat thus changing DOC release.

In this chapter, a year and half of stream water samples from post-blocking periods in the study site, which we collected by the author and pre-blocking samples by Turner et al., (2013) to access a total three and half years drain blocking project conducted in northern English upland. The aim of the project is to test whether the blocking effects the DOC export and concentration changes and whether the blocking effects upon DOC would be effected by different catchment scales.

2.2 Methodology

The approach of this study was to test the effect of drain blocking on the release of DOC from peatland in the UK. In the study, two sets of paired catchments have been observed for a year prior to any blocking, one set of drains was then blocked and the other left open, both the open and blocked set were then monitored for three subsequent years. In each set of drains there were two zero-order drains and a first-order drain, the zero-order drains both feeding into the first order drain in each set. One of paired sets of catchments was blocked as a treatment, while the other set remained unblocked as a control. Therefore, the study allows comparison assessments in parallel controls of two scales of catchments during several years. At the end of this period of monitoring a tracer experiment was conducted.

2.2.1 Study site

The study location was located on Cronkley Fell, an area of moor used for grouse shooting and sheep grazing. The area was managed using rotational burning (Turner et al., 2013). The six catchments share a common watershed and were divided into two sets of nested catchments: the first set catchment is left unblocked through the whole study as the control (National grid reference NY 83140 27284, Figure 2.1) at an altitude of 520 m above sea level; the second set, which were blocked after one year using peat dams, were used as experimental catchment, where located at an altitude of 570 m above sea level (National grid reference NY83800 26996). The underlying geology of the catchments is a succession of limestones of the Great Scar Limestone group. The vegetation of the catchments is dominated by *Eriophorum spp*. (cotton grass), *Calluna vulgaris* (heather) and *Sphagnum spp*. (moss).

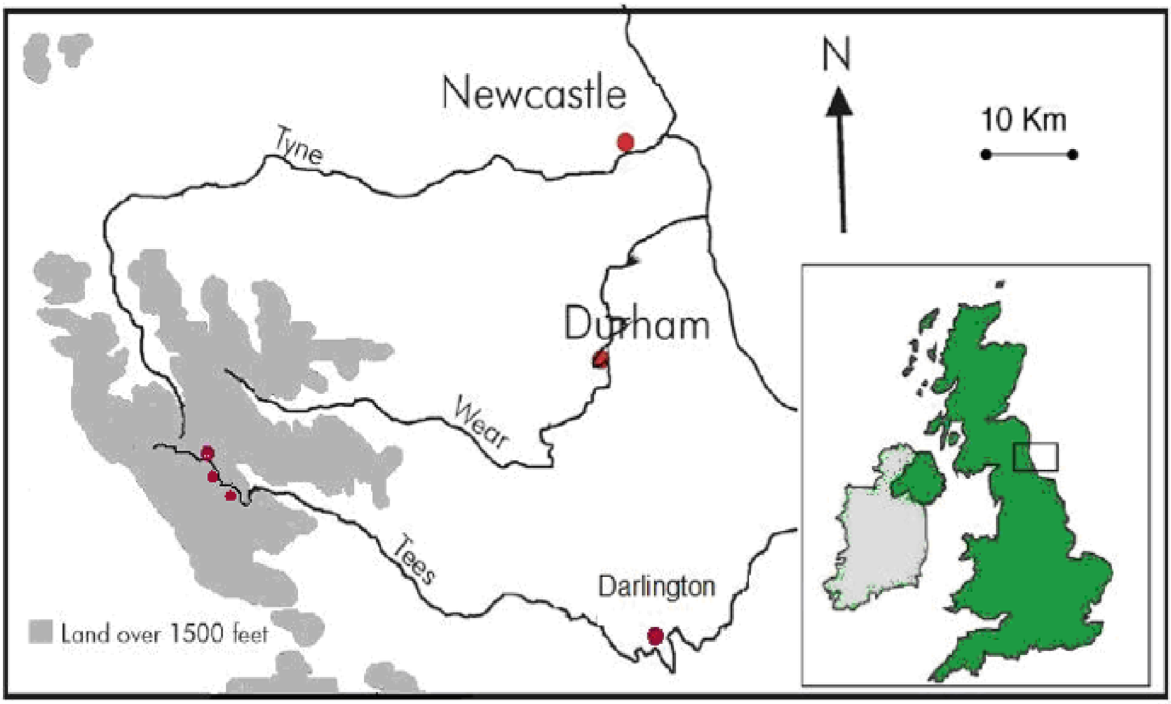

Figure 2.1: Location of Monitoring Sites in Upper Teesdale (Turner, 2012).

Figure 2.2: Blocked drain in Cronkley Fell looking, north west to the Cowgreen Reservoir, October 2010

Within the context of two large catchments, individual ones can be monitored. For the control set, first orders drain (CR3) and zero-order drains (CR1 and CR2) were monitored. The actual scale of each three drains was: 0.230 km^2 on CR1; 0.215 km^2 on CR2; 0.750 km^2 on CR3 (Figure 2.2 and Figure 2.3).

The experimental set of catchments follows a similar pattern to the control set, which also had two zero-order catchments (CR5 and CR6), and a first-order catchment (CR4). However, CR5 runs parallel to the rest of the site rather than flowing directly into CR4. The topographic characters of CR5 are with a small cross-sectional area and lack of feeder drains which means that CR5 has the typical characteristics of a zero-order drain. The other zero-order drain (CR6) flows directly into CR4. In this set, CR4 has a catchments area of 0.715 km^2, CR5 of 0.443 km^2 and CR6 of 0.305 km^2 (Figure 2.3).

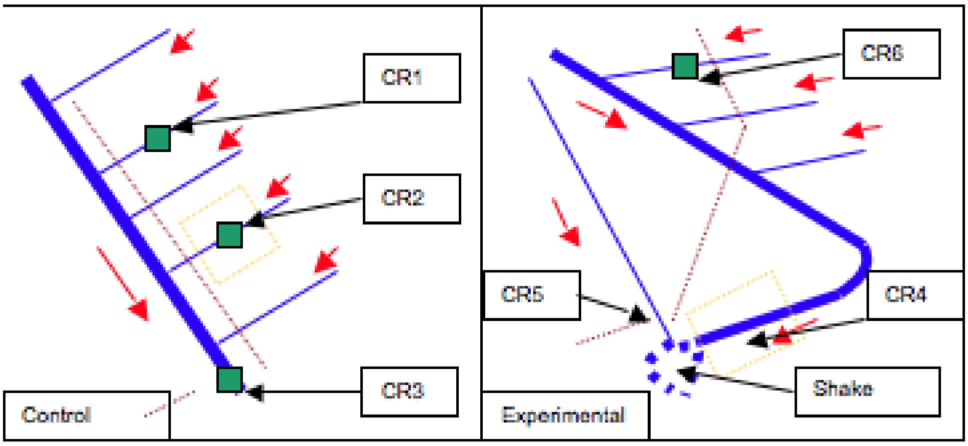

Figure 2.3: Schematic diagram of monitoring site layout on Cronkley Fell (Turner, 2011)

KEY   ***Monitoring site***   ***Flow direction***

First order stream   ***Soil water dip well network***

Zero order stream   ***Run off trap network***

2.2.2 Sampling Program

To calculate the DOC export from each catchment, a detailed sampling program was taken from 2011 to 2012, although data from the site were available form 2007 and discussed in Turner et al. (2013). The author was involved in the last year and half of field sampling and analyzed 1120 post blocking water sample, which are included in this chapter. In the six study catchments, an automatic water sampler was positioned and took samples of a frequency up to every 24 hours. It should be noticed that during later November to early January the heavy snow made it impossible to get the study site.

Once the samples were collected, they were then transported to the laboratory. If the samples could not be analyzed immediately they were frozen.

Figure 2.4 Display of V-Notch Weir and Autosampler in Cronkley, 2010.

2.2.3 Sampling Analysis

All samples collected from the field were analyzed for pH, conductivity, and absorbance. The significant amount of samples from the study site also makes the measurement of DOC concentration in every single sample impractical. Sample absorbance at 400 nm is typical for the humic fraction of DOC (Thurman et al., 1985) and was thus used for the basic colour reading. The E4:E6 ratio (Thurman et al., 1985), the ratio of absorbance at 465 nm and 665 nm, was used as a measure of DOC composition. Although there are some concerns of inaccuracy relating water colour to DOC concentration (Wallage and Holden, 2010), a total of 3945 samples were collected from the study site and 1125 samples collected from the field were selected to present the actual range of flow, weather and seasonal conditions. The selected samples were filtered through 0.45 µm filters and the DOC concentration measured using the colorimetric method of Bartlett and Ross (1988). The method relies on measuring the loss of colour by a Mn(III)-pyrophosphate complex as Mn(III) becomes reduced by organic carbon in the presence of concentrated H_2SO_4. A 1 ml aliquot of sample is used with 0.5ml each of H_2SO_4 and a manganese complex. Samples are left to incubate for 20 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.

In this study, a thin plate V-notch weir was constructed on each of the 6 selected catchments. The flow volumes of drainage water were measured using 1/2-90 degree V-notch weir (British Standards Institution, 1965). Instead of using sampling chamber to measure flow (Cuttle and Mason, 1987); a pressure transducer was connected to data logger and programmed to store the depth of the water every 15 minutes (Figure 2.4). The discharge of 1/2-90 degree V-notch weir, Q, is given by following expression (ISO, 1980):

$$Q = C_e * \frac{8}{15}\sqrt{2g} * \tan\frac{\theta}{2} h^{2.5} \qquad \text{eq. 2.1}$$

Where: C_e = the discharge coefficient for the weir, taken as 0.578 for the 1/2-90 degree weirs; θ = the angle of the V-notch; g = the acceleration due to gravity (taken as 9.81 m/s^2); h = the depth of water over the weir (m); Q = discharge (m^3/s).

2.2.4 Budget Calculation

Interpolation or extrapolation were commonly used in studies to provide continuous export estimates and then integrated to estimate total annual export (Littlewood, 1995). Extrapolation methods rely on the strong and significant relationships between the measured carbon flux and multiple, readily-measurable environmental driver variables (Clay et al., 2011). Interpolation is based upon the presence off strong seasonal components and assumed that the concentration measured in a water sample is representative of conditions in the river during the period between samples. Webb et al. (2000) used synthetic concentration time series to test a number of flux estimation methods and suggested that interpolation were generally more reliable than extrapolation method (Webb et al., 2000). Therefore, the strong seasonal component for DOC found in this study mean that interpretation was used to construct the budget.

There are wide range of extrapolation methods that have been proposed to calculate river fluxes from concentration and flow data (De Vries and Kalvers, 1994; Littlewood, 1995). However, a commonly used approach in carbon budgets of upland peats (e.g. Worrall et al., 2003) is to use ‘Method 5‘ of Littlewood et al. (1998):

$$L_5 = K \frac{\sum_{i=1}^{n} C_i Q_i}{\sum_{i=1}^{n} Q_i} \overline{Q_r} \qquad \text{eq. 2.2}$$

Where: C_i = instantaneous concentration; Qi = instantaneous flow; n = number of sampling the record; $\overline{Qr}$ = the mean river discharge over the period; K = conversion factor for the period of the record.

2.2.5 Statistical Analysis

This study was focused on the possible effects of drain blocking on DOC concentration and export. Both the scale and drain blocking have been assessed in consideration of impacts on DOC concentration and export. Further, water yield was considered as a covariate in DOC export . Thus the analysis of variance (ANOVA) was used to analysis the data here.

The factors considered in ANOVA were month of the year; site; drain-blocking status; and scales of catchment. There were 12 levels on Month factors each represent a month in a year. The site factor had 6 levels representing each monitoring site. The two sets of catchments left blocked and unblocked which means 2 levels in drain-blocking status. Then, the scales of drains had 2 levels, namely zero-order and first-order.

The existence of two sets of catchments makes it possible to consider the relative DOC concentration. The relative DOC concentration is calculated as the ratio between post blocking DOC concentration in both catchments. The ratios between the concentration of blocked drains and unblocked drains were given in case of eliminating any effects of natural variation on DOC concentration (for instance, the effects of year to year difference on DOC values). The ratio values were considered as per the first analysis.

The analysis of DOC export considered the above factors again. What's more, the water yield from each drain in that month was also taken as covariates.

Post hoc comparisons between factor levels were made using Tukey test and the magnitude of the effects of each significant factor and interaction were calculated using the ω^2 method (Vaughan and Corballis, 1969).

Besides the use of the ANOVA, the entire DOC exports dataset, between blocked and unblocked catchments, was analyzed by double mass analysis. Double mass analysis uses the curve between two cumulative values, x and y, and x is then plotted against y. The curves allowed estimation of whether the variables had followed the same trends over the course of the study period. Thus, any breaks in the slope of curve indicated a change in trend for one of the variables (Searcy and Hardison, 1960). Double mass analysis was firstly used to test the effects blocking has on the relationship between water yield and DOC fluxes, and then on the relative accumulation of DOC exports between two catchments. Whisker box plots were used across the entire thesis to give the visual illustration on the subjected changes. An animated example was given in figure 2.5 to distributed different sections of plots, where:

•A: upper whisker: represents the upper 25% of the distribution (excluding outliers)

•B: interquartile range box: middle 50% of the data

•C: median of the data.

•D: lower whisker represents the lower 25% of the distribution (excluding outliers)

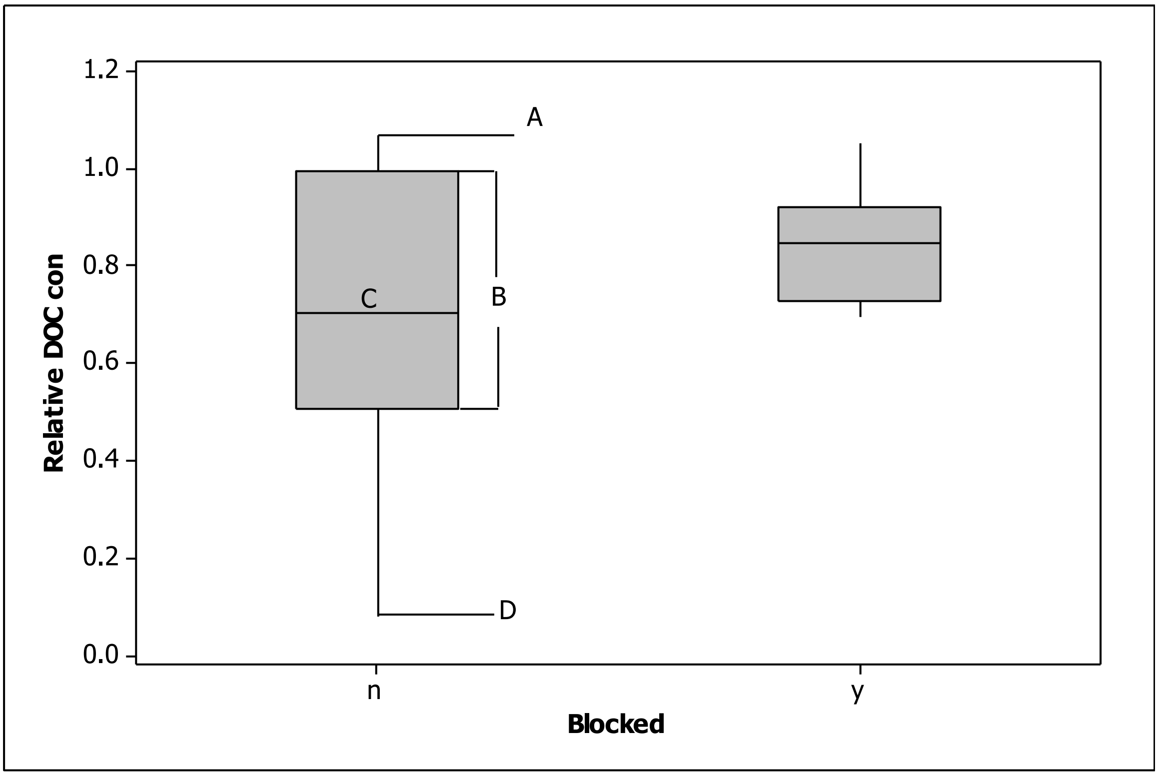

Figure 2.5: illustration of whisker box plot.

2.3. Results

2.3.1 DOC concentration

From August 2007 to April 2012, 5260 samples were collected from Cronkley. Of these, 3945 of them were analysed directly for the DOC concentration using the method of Bartlett and Ross (1988). For the rest of the samples the DOC concentration was calculated by calibration curve between DOC concentration and absorbency at 400 nm. On both the control and experimental catchment, DOC concentration changes were observed on different scale and site (Figure 2.6, Figure 2.7 and Figure 2.8).

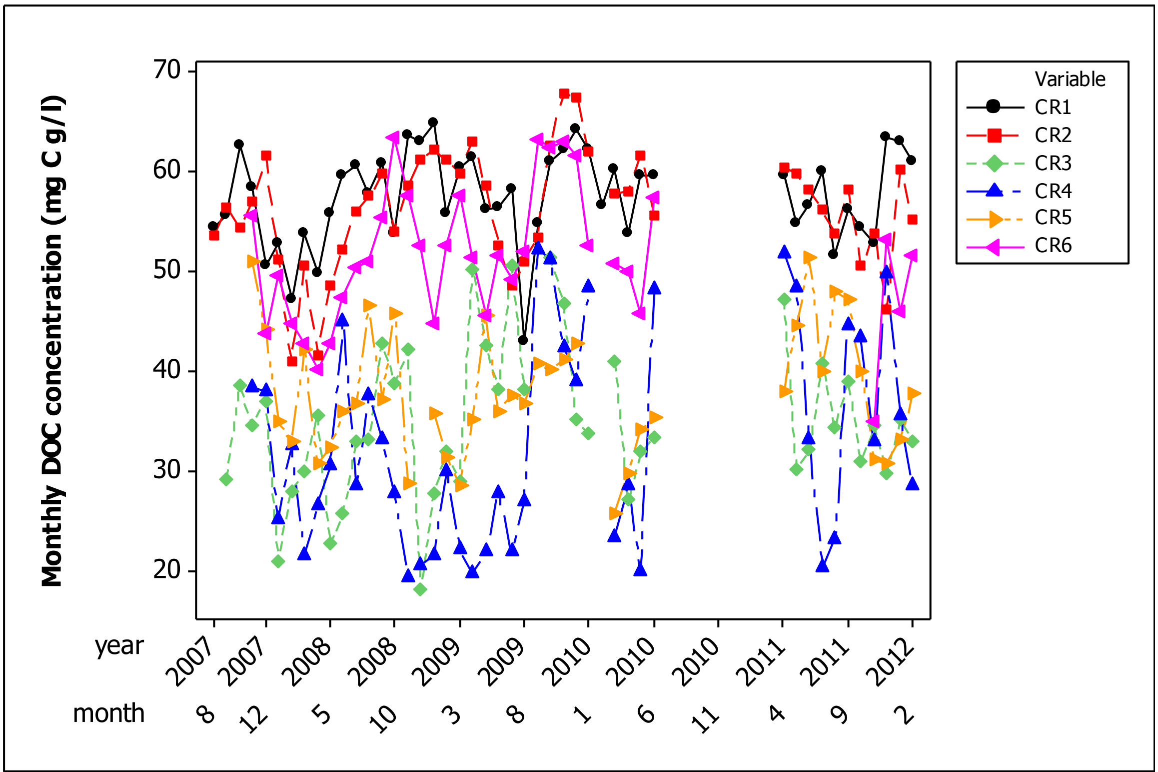

Figure 2.6: Time series of monthly DOC concentration of all catchments, where CR1- CR3 are control catchment; CR4-CR6 are experimental catchments. The access to study site was limited from June 2010 to April 2011, which left the gap in time series. The units of DOC concentrations are mg Carbon per g soil per liter sample.

Analysis of the monthly time series (Figure 2.6) for all the monitored sites shows a strong seasonal cycle with the increase of DOC concentration during spring and summer. A reversed relation between scale of drain and DOC concentration was observed throughout the study periods. Differences between different scales of drains can be observed on the time series (Figure 2.6). For instance, CR1 and CR3 in the control catchment (Black and Green line in Figure 2.6); CR4 and CR6 in the experimental catchment (Blue and Pink line in Figure 2.6) both observed an average of 22 mg C g/l increase from first order drain to zero order drain.

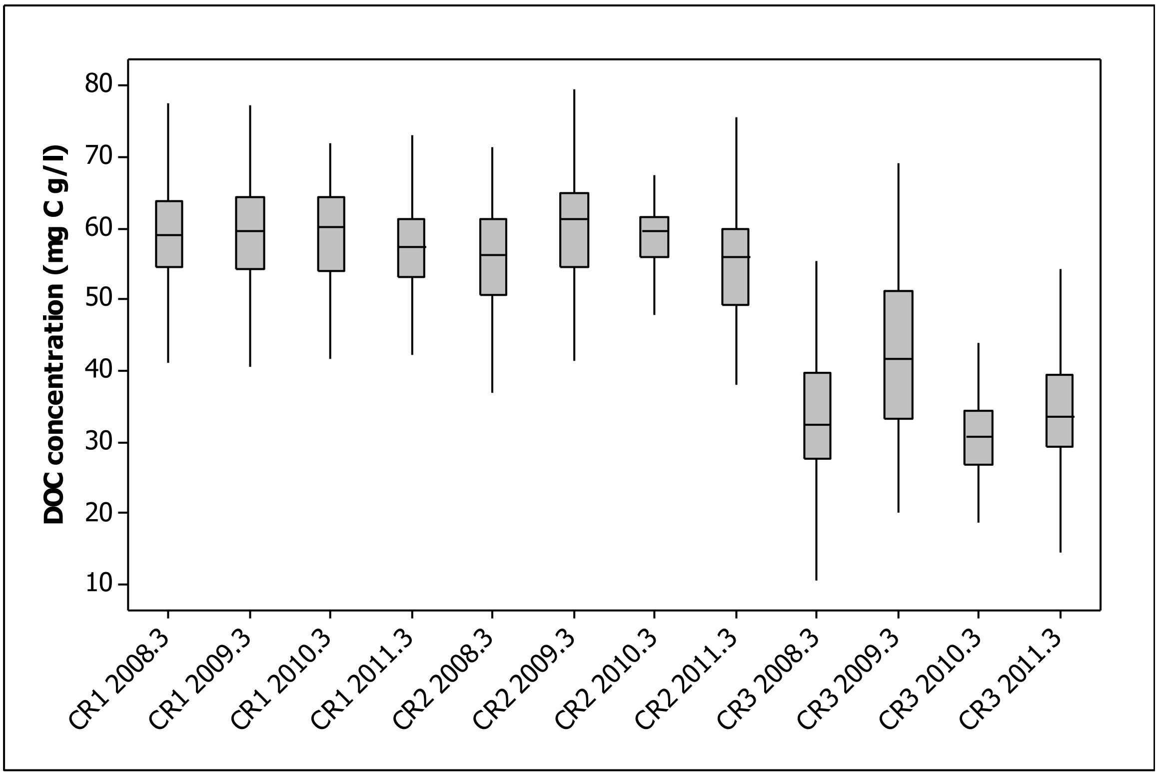

Figure 2.7: The box plot of DOC concentration of control catchment on Cronkley Fell.

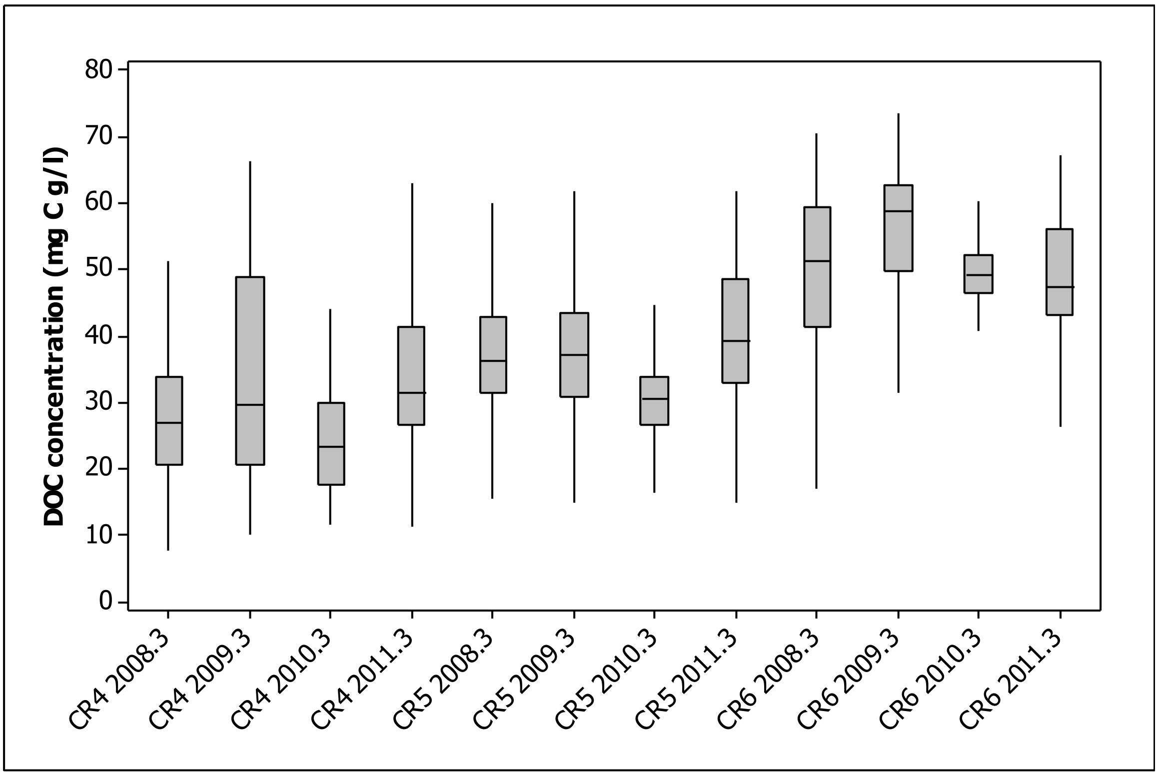

Figure 2.8: the box plot of DOC concentration of experimental catchment on Cronkley Fell.

The concentration of dissolved organic carbon in the control catchment increased with increasing scale (i.e. CR1, CR2 - zero-order catchment, CR3 - first order catchment). A notable concentration increase was observed between zero and first order drains (Figure 2.7), which might be the result of a combination of various processes. Firstly, natural DOC degradation may have occurred as water moved down the catchment. However, earlier studies of DOC degradation showed that these influences were small and cannot be the main reason of DOC concentration decrease (Turner et al., 2013). Secondly, the DOC concentration may dilute with increasing large amount of water from low DOC sources being added into the system. It is suggested that with two reasons combined together, the observed decrease of DOC concentration may be explained.

The DOC concentration of experiment catchment also showed a decrease with increasing scale (Figure 2.8). Again this can be explained by a combination of the effects of dilution and DOC degradation. A slight increase was observed in the drains after blocking. The median

DOC concentration change caused by blocking was an increase of between 3% and 23% between zero and first order drains. The reason for this increase might be the effects of the periods of monitoring, as concentrations may naturally fluctuate from year to year independent of blocking status (Turner et al., 2013).

The ANOVA of DOC concentration data found that all these factors were significant at least at the 95% probability and explain 42.5% of the original variance in the dataset. It should be noticed that error term here explained 59.2% of the original variance. This high proportion of the original variance due to the error term may not be just because of a matter of measurement and sampling error, it could, for instance, represent some unknown interaction between influential factors or covariates that could not be included in the ANOVA. The lower P values in Turner et al. (2013) were all zero, which indicated the factors involving in this study were more sensitive (Table 2.1) and this was probably due to the additional data over the extra year since the study of Turner et al. (2013). The proportion of variance showed that blocking explained a considerable proportion of the variance (10%), which previous work didn't find any significant influence for (Turner et al., 2013). This significant change could be the result of various reasons; for instance, increased sample size and time may increase the sensitivity of ANOVA. Among the three factors, the most significant factor was scale, which explained 27% of variance. The interaction of scale and month was significant, however it explained just 1% of the variance. Still, the presence of significant interactions between month and scale showed different seasonal cycles for first and zero-order streams.

Source	P	Portion of variance (%)
Month	<0.001	3.65
Scale	<0.001	27.18
Blocked	<0.001	9.94
Month*scale	<0.001	1.05
Error	58.18	

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

2.3.2 Relative DOC concentrations

Compared with the control catchment, it is clear that the experimental catchment has higher DOC concentration at all scales (Figure 2.8). This is similar to that observed by Turner (2011). At the first order scale, drain blocking appears to have suppressed the range of relative DOC concentrations compared to the unblocked catchment. Drain blocking effects were observed on both zero and first scale. There was a 4% reduction of relative DOC concentration on first order drain (Figure 2.9) and 2.9% reduction on zero order drain (Figure 2.10) upon drain blocking.

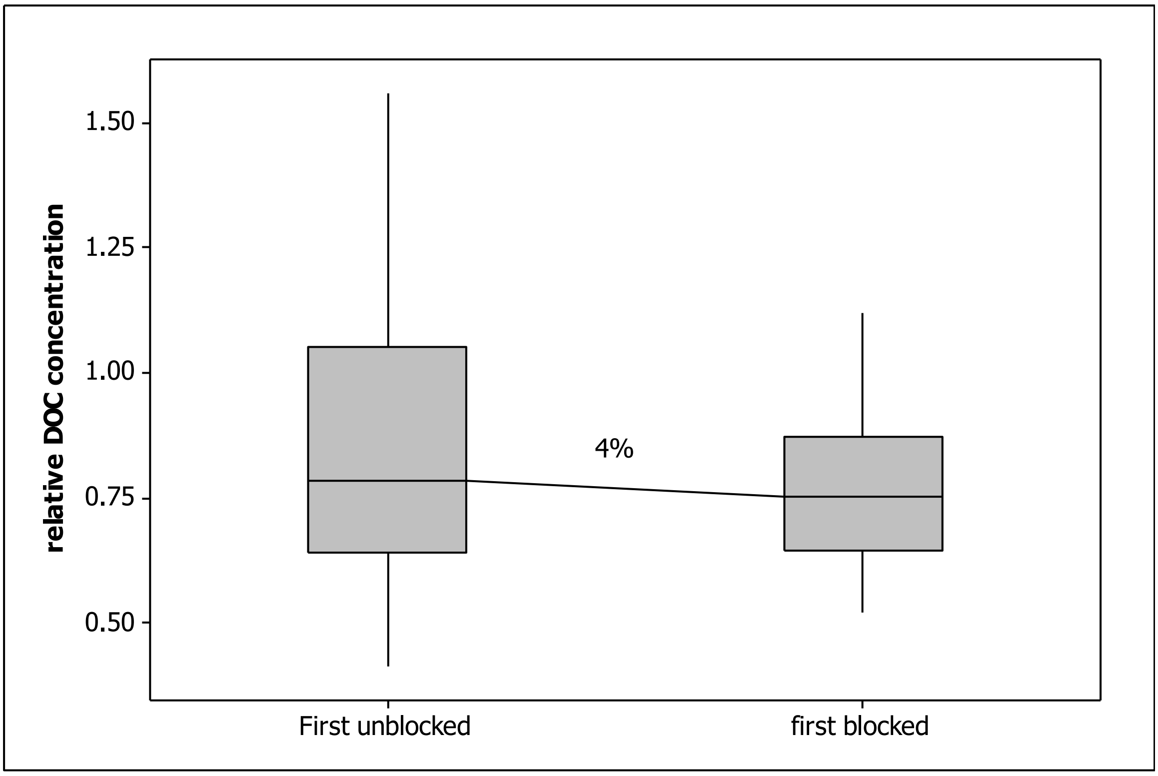

Figure 2.9:The box plot of relative DOC concentration at first order catchment.

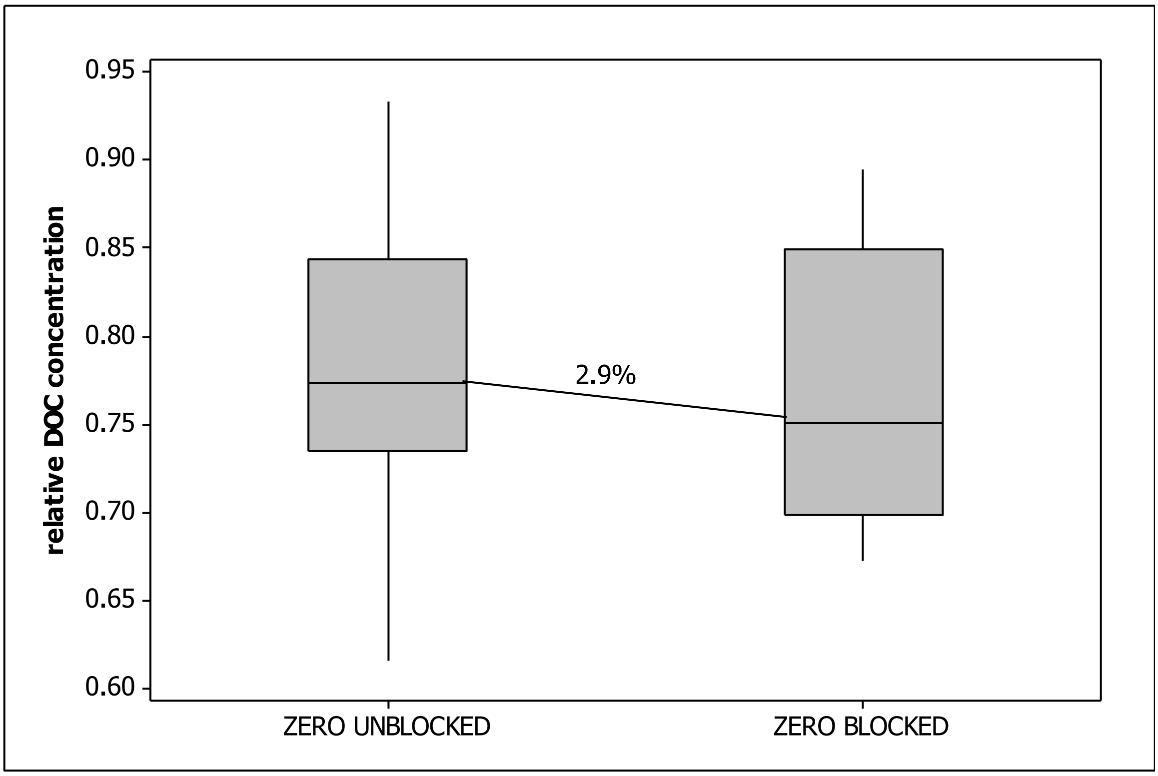

Figure 2.10:The box plot of relative DOC concentration at zero order catchment.

ANOVA was performed on the relative DOC concentration factors, which included the factors of blocking status, scale, and the interaction between blocking and scale (Table 2.2). Using relative DOC concentration eliminated the effect of seasonal differences and the ANOVA showed that the scale factor was insignificant (Table 2.2). However, the interaction between scale and blocking was found to be significant and explained 38.3% of the variance in the dataset. This highlighted the possibility that blocking may be having an effect on DOC concentration as scale changes. The majority of the variance in the dataset was explained by blocking status: estimated at 42% of the original variance. The error term was about 20%, which is a large decrease compared to the earlier analysis, which was 49.4% (Turner et al., 2013). It also shows a reduction compared to the actual DOC concentration in this study and shows the usefulness of the relative DOC which can eliminate a considerable proportion of the unaccounted for natural variation. The ANOVA difference between DOC concentration and relative DOC concentration here highlighted the reliability of relative values.

Source	P	Portion of variance (%)
Scale	0.212	0
Blocked	0.008	42.24
Scale*Blocked	0.01	38.83
Error		18.92

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

2.3.3 DOC Export

The measurement of DOC export (g Carbon per m^2) is the mass of DOC leaving the observing catchments per unit area. The data were available from August 2007 to April 2012, which including both annual and monthly results.

There is an observed reduction in DOC export between the pre-blocking and post blocking state. The annual DOC export reduction was recorded at all sites (Figure 2.11). The reduction size varied with the change of site and scale. The result showed that reduction was about 3% at zero order drain on control catchment and 0.65% on first order drain. This reduction based on the control catchment reflected the natural year-to-year changes of DOC export. Whereas the reduction observed on experimental catchments were 10% at zero order drains and 2.56% at first order drain. This reflected the combination effects of nature year-to-year variance and the effects of blocking on DOC export.

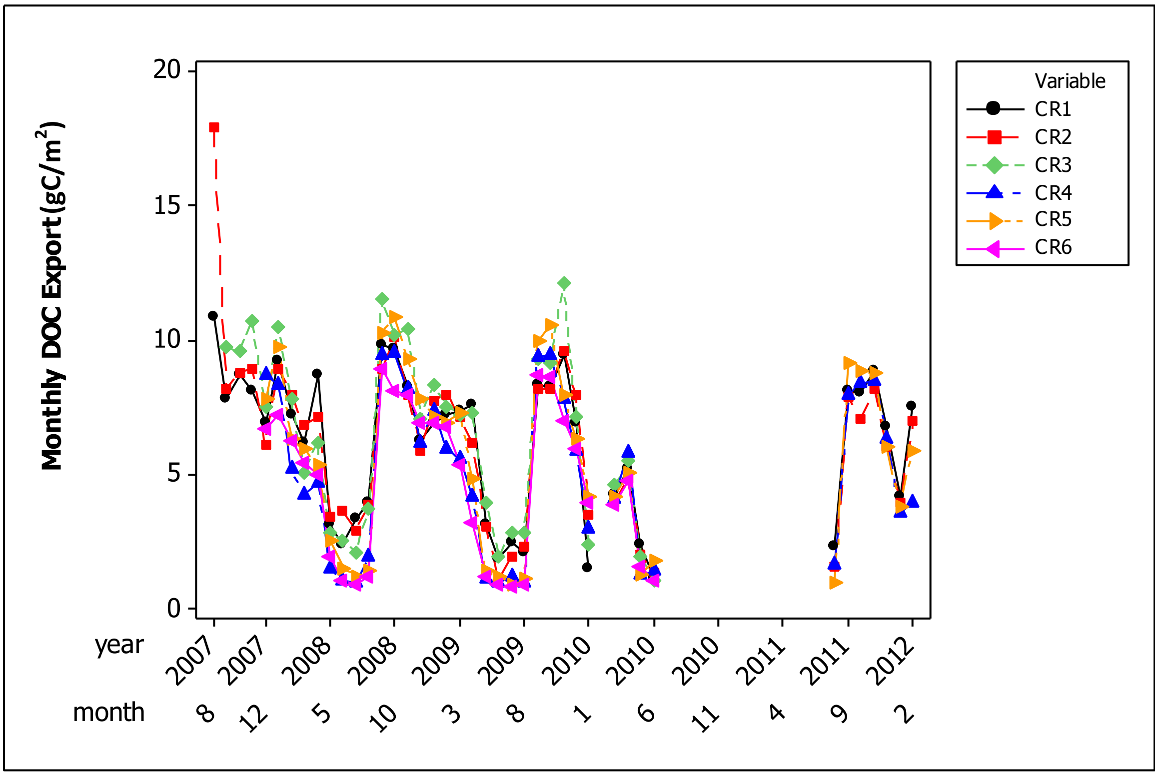

Figure 2.11: Monthly DOC export time series for all sites.

ANOVA was performed with and without covariates. In this analysis, water yield was used as a covariate. When the ANOVA was performed without water yield as a covariate, month of year, scale, blocking statues and interaction of blocking and scale were found to be significant (Table 2.3), with the majority of the variance being explained by the month of the year and a increase rate of error term of 16.2%.

Source	P	Portion of variance (%)
Month	<0.001	96.27
Scale	0.489	0
Blocked	<0.001	3.73
Scale*Blocked	0.933	0
Error		0.002

Table 2.3: ANOVA of DOC export for all monitored sites and months giving the probability of the factor/interaction and portion of variance explained by the factor without covariant.

Source	P	Portion of variance (%)
Water Yield	<0.001	88.21
Month	<0.001	11.49
Scale	0.492	0.22
Blocked	0.286	0.04
Scale*Blocked	0.238	0.04
Error		8.79E-05

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

It was found that when water yield was included in the analysis, water yield, site month of the year, blocking status and the interaction of blocking and site are all significant and together explained 89% of the original variance, i.e. the error term explained only 11% of the original variance. Water yield, as a covariate, explained the majority of the variance in the data set (88%, Table 2.4). However, the significance of water yield as covariance is that export includes flow in its calculation and so it's self-correlated. It should be noticed that month factor also explained 11.4% of variance, which highlighted the seasonal change as an influence on the DOC export. Besides the variance of water yield, it is rare to find that the blocking (0.04%) and scale (0.22%) did not show a big influence on actual DOC export (Table 2.4).

Site	Catchment/Scale	TAE	MAE	Change in DOC Export (%)
CR1	Control zero-order	78.54	76.21	-2.96
CR2	Control zero-order	77.97	75.62	-3.01
CR3	Control first-order	80.44	79.91	-0.65
CR4	Experimental first-order	61.57	59.97	-2.56
CR5	Experimental zero-order	72.7	65.81	-9.47
CR6	Experimental zero-order	62.56	55.02	-12.05

Table 2.5: The percentage change in total annual DOC export when the total annual DOC exports from the pre-blocking year is compared is compared to the mean annual total DOC export from the three post blocking years.
Where: TAE=Total Annual DOC Export: Pre-blocking year (tC/km^2), MAE=Mean Annual Total DOC Export: Post-blocking years (tC/km^2).

A plot of DOC export against water yield for the zero order sites in the experimental catchment demonstrates a clear reduction in the DOC export caused by the blocking (Figure 2.12). However, this decrease was not observed on the first order drain on the experimental catchment (Figure 2.13). It is possible that the bypass flow around the zero order drain blocks was adding additional water to first order drains, which initially suppressed DOC export on this scale. The mixing effects of additional water source and any dilution effects from alternatively sources of water would disrupt the expected linear relationship between water yield and DOC export at this scale as seen in Figure 2.10. Also the combined effects with additional water sources, dilution and DOC degradation might be acting at this larger scale. The presence of any component of bypass flow or external water source will reduce the efficiency of any blocking.

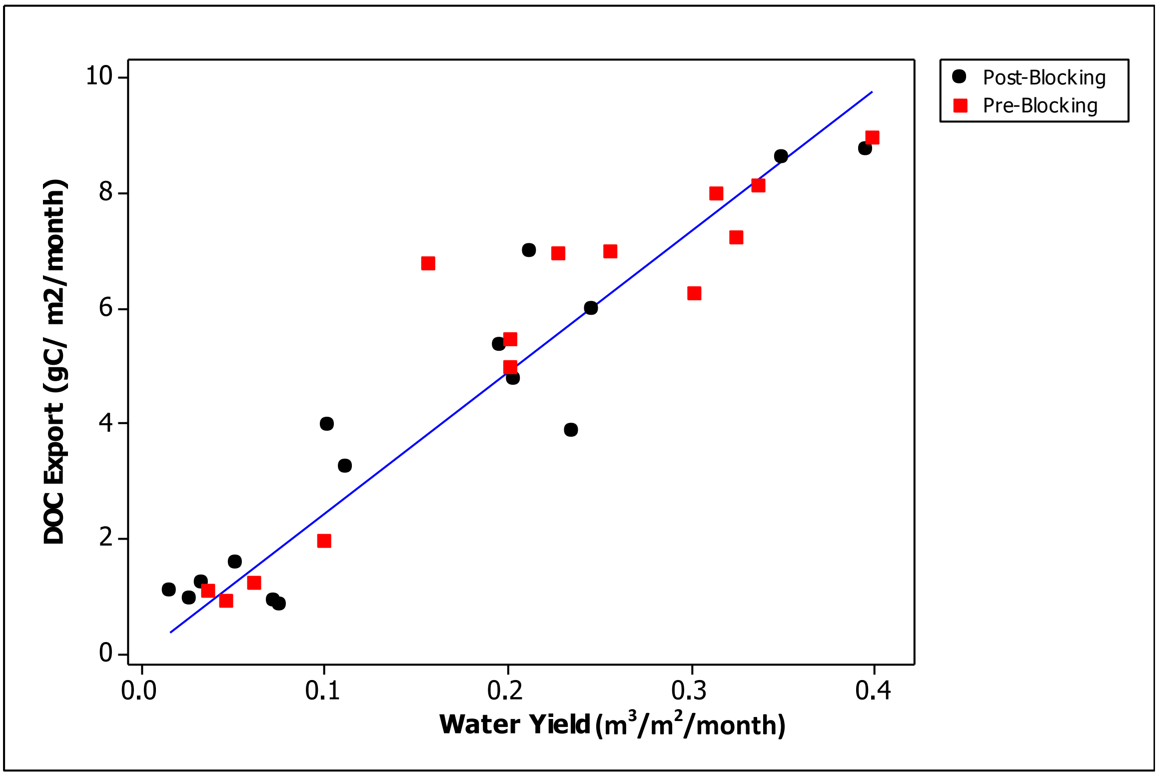

Figure 2.12: The correlation between water yield on DOC export at zero order scale for experimental catchment. Trend line: y=0.465+22.7x, R2=0.88

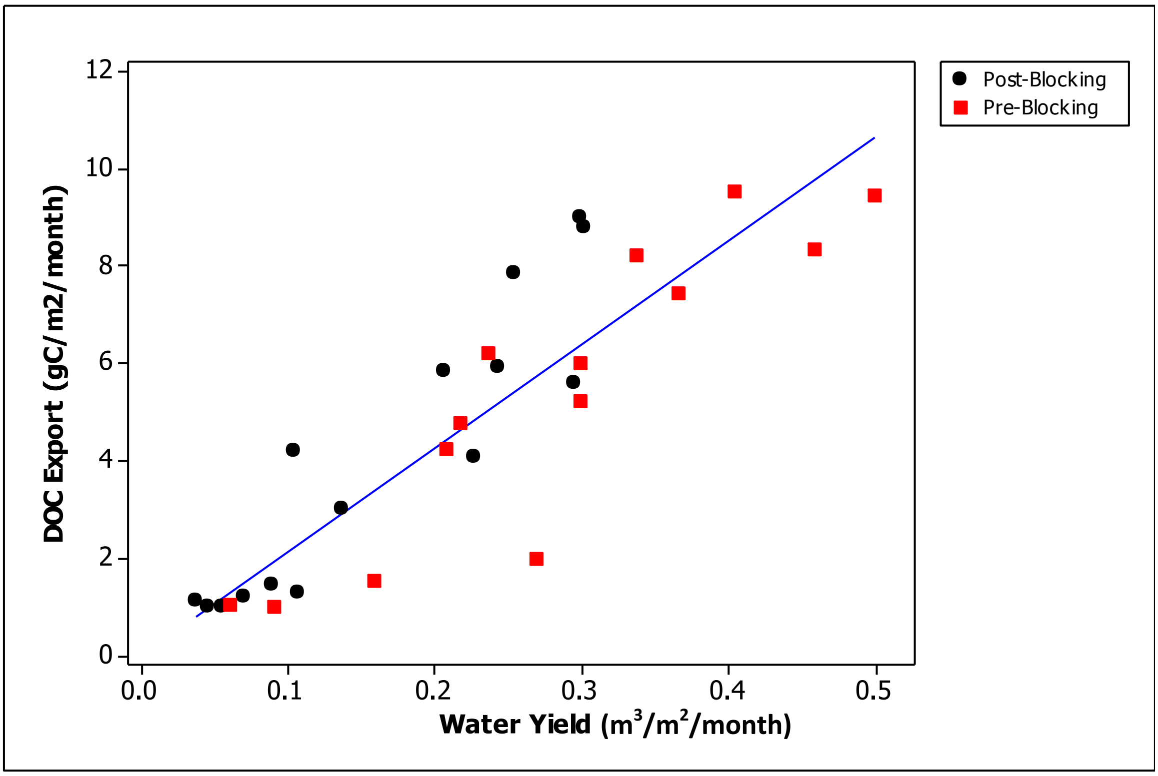

Figure 2.13: The correlation between water yield on DOC export at first order scale for experimental catchment. Trend line: y=0.057+21.2x, R2=0.78.

2.3.4 Relative DOC Export

The comparison of the DOC export between catchments (Figure 2.14) shows that at all scales that the control catchment has higher DOC export than experimental catchment.. A clear reduction in relative DOC export was observed between the blocked and unblocked catchment at all scales, but the reduction was larger at the first order scale with 7% reduction and 12% reduction at zero order drains. When ANOVA was performed on the relative DOC export data; it was found that water yield, month of the year, scale, blocking and interaction of scale and blocking were significant and in total explained 83.7% of the original variance (Table 2.6). The error term explained 16.2% of variance. As above with the DOC export, water yield still explained about 94% of the variance whereas the scale, blocking and interaction between both explained the rest of the original variance in the dataset. This comparison between water yield and other factors indicated how those decreases in DOC export recorded post blocking are mainly controlled by reduction of water yield than DOC concentration.

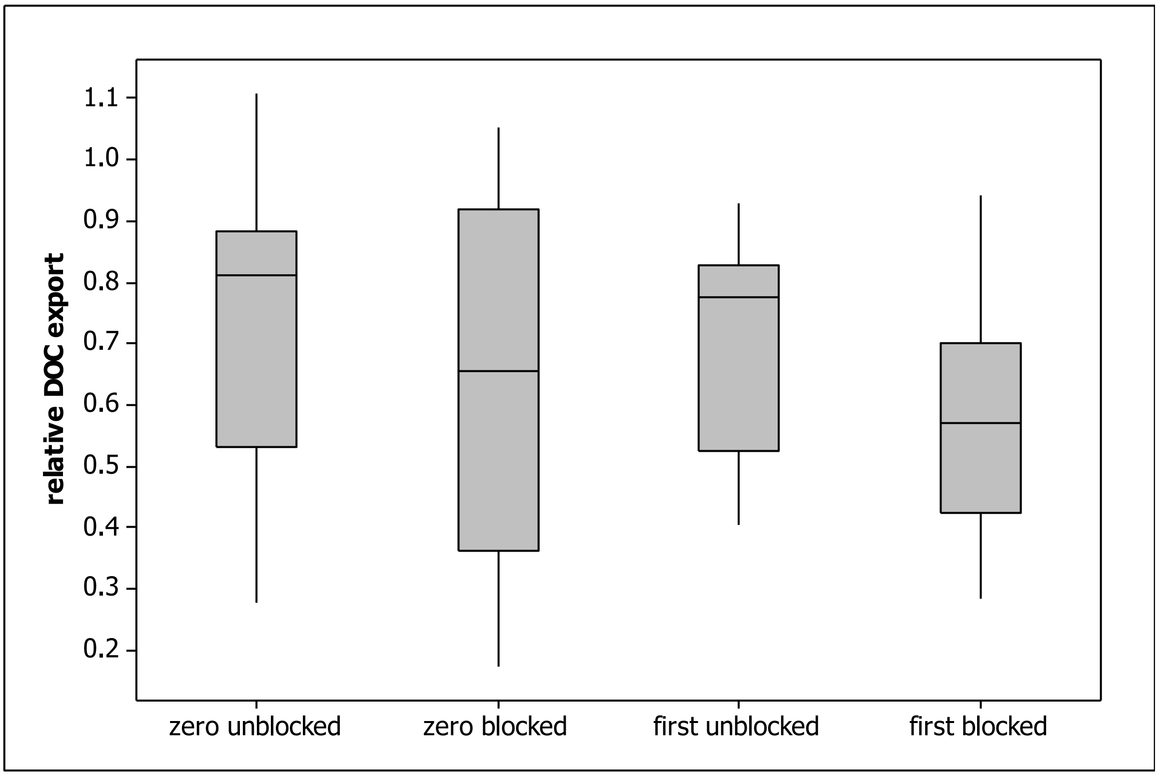

Figure 2.14The box plot of relative DOC export at zero order and first order catchment.

Source	P	Portion of variance (%)
Water Yield	0	94.65
Month	0.193	0.98
Scale	0.003	1.83
Blocking	0.009	2.34
Scale*Blocking	0.222	0.18
Error		0.00092

Table 2.6: ANOVA of relative DOC export for all monitored sites and months giving the probability of the factor/interaction and portion of variance explained by the factor.

2.3.5 Double Mass analysis

A linear trend is apparent in the double mass curve between cumulative monthly DOC flux in both control and experimental catchments (Figure 2.15 and Figure 2.16). An instant change on the slope of the double mass curve was observed on the zero order drains (CR5 and CR6) of the experimental catchment at the time of drain-blocking. The curve change is clearly showed that a DOC change occurred post-blocking (Figure 2.15). Although the first order drain (CR4) doesn't show the instant break like others, it is possible to show a continuing decrease on DOC flux with the increasing water flux in future observation (Figure 2.15). There is no slope break observed on the double mass curve for the control catchment where no drain blocking happened (Figure 2.16). This excludes the possibility that the slope break in the double mass curve for the experimental catchment was due to a common change in both catchments.

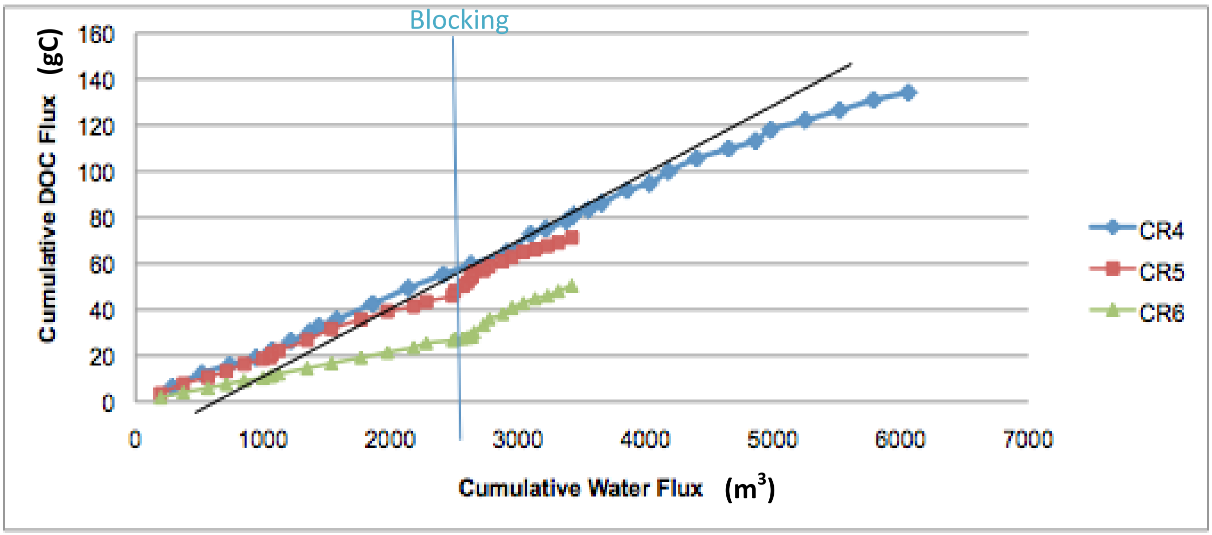

Figure 2.15: Double Mass Curve for Cronkley Experimental Catchment. Blue Line represents the start of blocking. Where the Blue line shows the start of blocking.

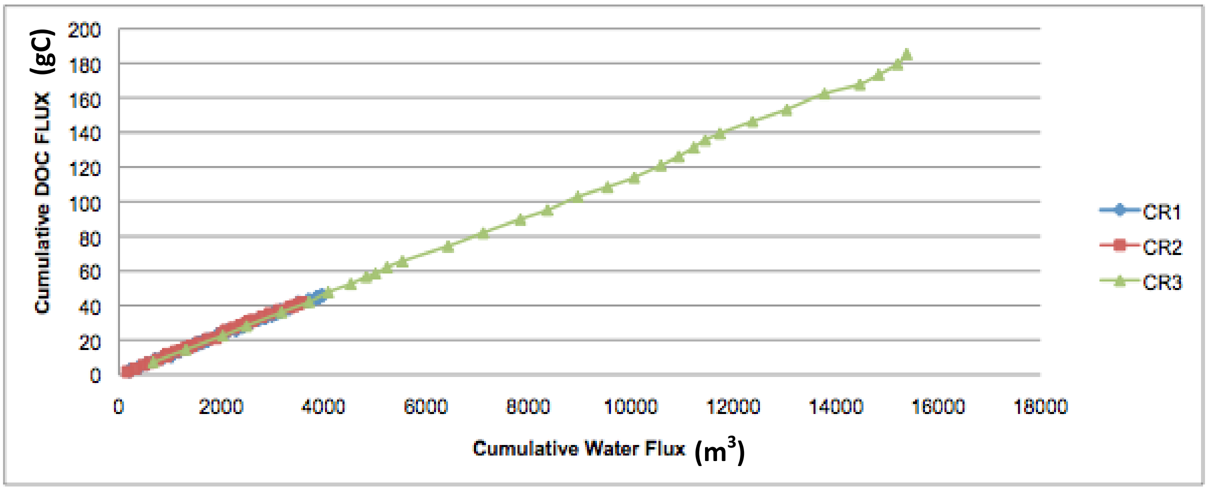

Figure 2.16: Double Mass Curve for the control catchment on Cronkley Fell.

Seasonal effects could be seen on all double mass curves (Figure 2.15). However, a instant slope break on zero order drains and a constant slope on first order drains post blocking were not accompanied by any similar reduction in the control catchment. Therefore, it is clear that the changes in slope between different drains on the experimental catchment were an effect of a change in DOC regime post blocking. Further, the changes could be observed on the double mass curve for the same scale both on control and experimental catchment (Figure 2.17 and Figure 2.18). Figure 2.17 indicates a change in export values between the two drains with DOC export maybe expected accumulating more rapidly on the blocked drain if further breakthrough of slope occurs (CR1). Thus, drain blocking did show an influence on the zero order drain of experimental catchment. For the first order drains, a lack of continuing records makes it difficult to judge whether the observed potential reduction could be seen as an effect of blocking or not. To evaluate the overall effects of drain blocking on experimental catchment therefore needs further study.

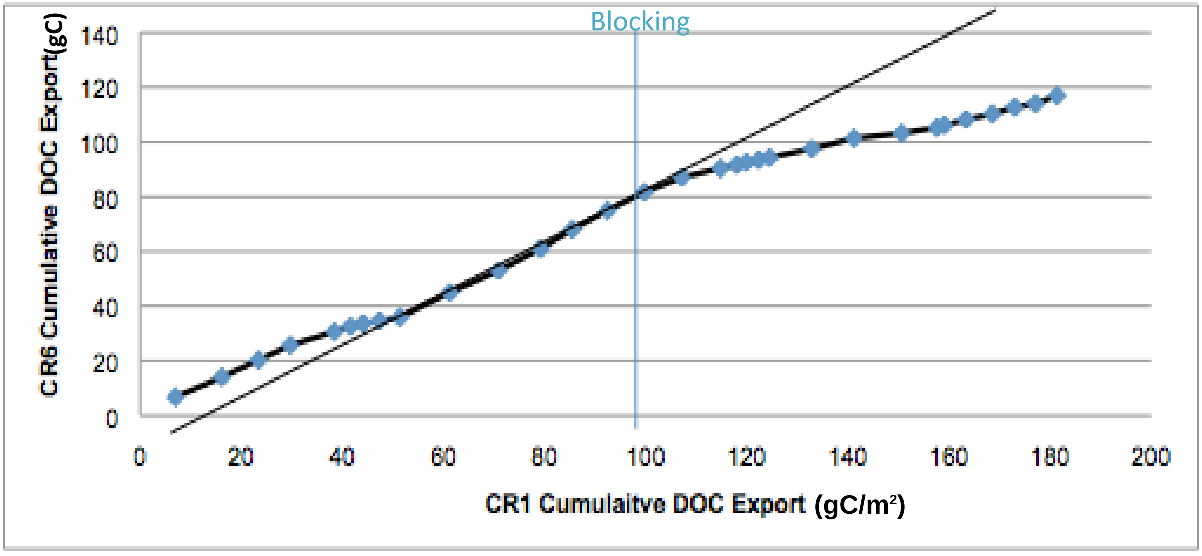

Figure 2.17: Double Mass Curve for DOC export on zero order in both control and experimental catchment. CR1, control catchment; CR6, experimental catchment. The black trend line indicates the straight linear trend from which the curve is tending away. The data point represent cumulative monthly intervals. The blue line represents the start point of blocking.

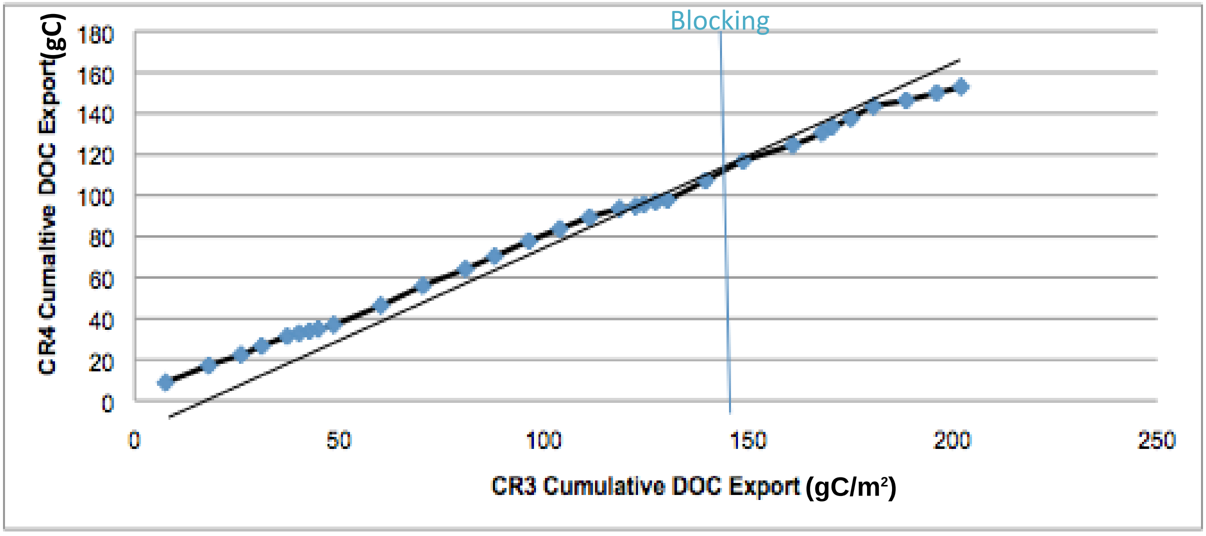

Figure 2.18: Double Mass Curve for DOC export on first order in both control and experimental catchment. CR3, control catchment; CR4, experimental catchment. The curve does not tend away from the trend line post blocking. The data points represent cumulative monthly intervals. The blue line represents the start point of blocking.

2.4 Discussion

Evaluation of DOC release from peat bog in Cronkley Fell was based on four years of observation. Both actual and relative values were used to show the change of DOC behavior in this peat bog. It was found that relative values, which could eliminate the natural year-to-year variance, were more sensitive than actual values. The reduction of DOC concentration and DOC export were observed on both first order and zero order drains, however, the size of the reduction was only 2.2% on the zero order and 4 % on the first order drain.

At different scales, the reduction of DOC concentration was observed, but the drain blocking effects were not as big as might be expected. A small fluctuation was observed both on the control catchment and experimental catchment. The ANOVA suggested the biggest contribution to this reduction is the natural seasonal change rather than blocking. Use of relative rather than absolute values can eliminate the effects of year-to-year natural changes effects on the DOC values. A reduction still exists on both catchments. It is comparatively small at only 2.9% on zero order drains and 4% on first order drains. It also should be noticed that with the increasing of the scale the DOC reduction is bigger. The difference between DOC reductions at different scales indicates that the effects of drain blocking may get bigger at larger scales. However, this difference with scale may not be a result of drain blocking; it may be caused by the potential water sources that adding into the first order drain. The large amount of extra water may increase the water table and therefore cause the dilution of DOC concentration on first order drains. Apart from the scale effects on the DOC concentration changes during study, the observed positive DOC concentration decrease can be speculated to be duo to the DOC concentration being strongly related to water table. This speculation assumes that if there is observed significant water table changes, it would be expected to show as observed DOC concentration changes.

The controversial point is that there was not an observed significant water table change, which may indicate other possible reasons that increase DOC export. For instance, the potential water bypass sources, which were adding DOC to the study catchment

According to the observed water yield data in DOC export, it is also showed it is the water table, instead of the blocking, explains the large part of variance of DOC export where the water table explained 88.21% variances of ANOVA of DOC export and blocking factor only explained 4% variances. It is clear that the DOC export followed the change in the water yield rather than the drain blocking.

2.5 Conclusions

Drain blocking on Cronkley Fell based on four years observation from 2008 to 2012, has shown that DOC concentration did decrease upon drain blocking. However, the effect of drain-blocking was lower at larger catchment scales. Result of observations showed that there is a 4% reduction of relative DOC concentration on first order drain and 2.9% reduction on zero order drain; 12% reduction on zero order drain for relative DOC export and 7% on first order drains. This clearly showed that the effect of drain blocking was decreasing with increasing scale.

Chapter 3 Events analysis

3.1. Introductions

There are several reasons why the study of storm events is of increasing interest to upland peat and hydrology research. First, the transportation of dissolved organic carbon (DOC) from soil systems to the aquatic system remains an important part of the carbon cycling. Numerous research studies have reported the increasing DOC concentration in upland catchments draining peat soils (Worrall et al., 2004, Wilson et al., 2011) and the majority of this DOC export is during storm events (Clark et al., 2008). Second, studies of storm events give insight into the flowpaths and sources of DOC within the catchment (Worrall et al., 2007, Austnes et al., 2009). During the hydrological peak, the DOC export is controlled by either the dilution from direct rainfall or interactions with the peat matrix (Holden et al. 2011). The interactions between different flowpaths can lead to variations in the concentration and composition of DOC leaching to the surface water between and during events. Besides the flow pathways, Pearce et al. (1990) found that event water contributions to storm flow increased with increasing drainage area. Brown et al. (1999) found peak runoff increased significantly with increasing catchment area, whereas the event-water contributions at the hydrography peak decreased significantly with increasing catchment area for all but the most intense rainfall events.

The mix of flowpath determines surface water chemistry during and after the peak flow events (Brown et al. 1999). End-member mixing models of various kinds have been used to understand the sources and pathways in catchments (Christophersen and Hooper, 1992). Worrall et al. (2003) used two end-member mixing model to assess old versus new water contributions to runoff in the peat catchment, however, three and four end-member analysis have also been also used (Worrall et al. 2006). Further more, the interpretation between the principal components analysis (PCA) and end-member analysis (EMMA) has been widely used in the study of peat-covered catchments (eg. Worrall et al., 2006). This study used PCA to understand the composition and sources of events water between managements in a peat-covered catchment.

As observed in the previous chapter, the concentration and flux of DOC observed as a result of drain blocking will change with scale of catchment and the blocking may alter the flowpaths operating during an event. For example, the blocking of drains could lead to longer residence times in the catchment. Therefore, an event analysis was conducted to assess different flowpaths. PCA and EMMA were conducted on the hydrological characteristics of the events. The same analysis included a range of chemical parameters to aid the investigation of the concentration changes during the events. ANOVA was used to determine whether drain blocking had an effect during the events.

3.2. Methodology

Events recognition exploits the outputs of hydrological changes as well as changes in DOC concentration and DOC flux in order to detect changes due to drain blocking. The analysis is based on characterising individual flow events using a range of hydrological data and including DOC flux and concentration changes over the subsequent days.

The approach of this study was to include non-events in the analysis, i.e. the event analysis started with consideration of rainfall events and if they did not result in a measurable runoff event then this was recorded as a non-event. The events analysis was based on the data collection used in chapter 2, where three years drain blocking analysis was conducted. The final data set considered one year pre-blocking data from January 1st, 2008 to February 28th, 2009 and two years post-blocking data Match 1st, 2009 to April 1st , 2010.

Storm hydrographs for each flow gauge were plotted against rainfall, and standard parameters were measured either from hydrograph or calculated from the time series.

The parameters were (Figure 3.1):

1. Rainfall characters

Each individual rain storm was described by the total rainfall of the day (mm), the rainfall duration (hours),and peak rainfall intensity (mm/hour).

2. Flow characters

The flow characteristics considered were: the flow lag time (hour), peak flow of the day (m^3/s), and the antecedent flow (m^3/s). Therefore, the analysis gathered the information of flow conditions of two days during a single event and linked the flow condition with next day's DOC concentration and flux changes.

3. Time since previous event

The time between events was included in the analysis whenever possible. However, due to heavy snow conditions; changes in the fledging season and equipment failure, there are gaps in the record which meant that it was not always possible to measure the actual time between events.

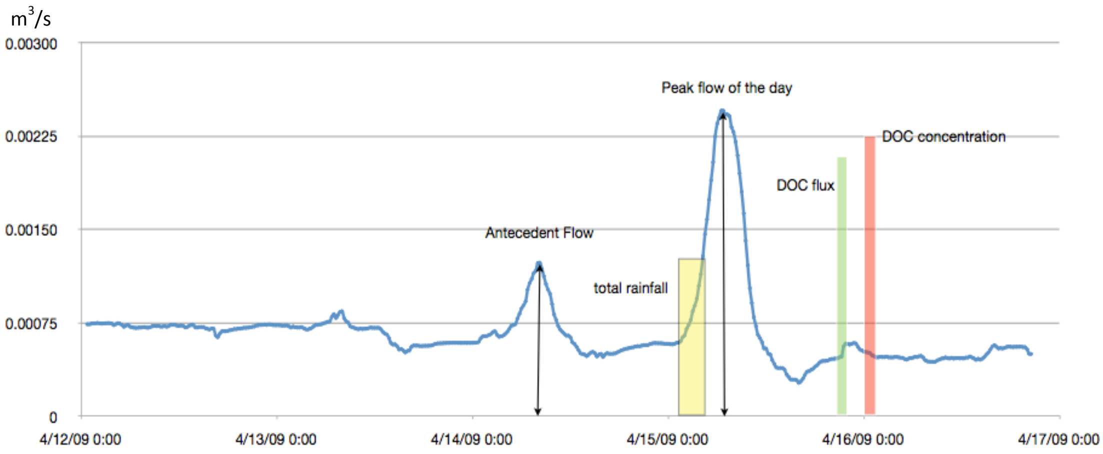

Figure 3.1: Deconstruction of hydrograph for event analysis showing the characteristics considered.

Events analysis was also performed with the consideration of the DOC concentration changes and DOC flux changes which were calculated from water samples before and after the rainfall events. The DOC concentration changes and flux changes were calculated from water samples taken from the autosampler in the field. As mentioned in earlier chapters, the sampling was programed to take samples every 24 hours. That means the DOC concentration were selected only 24 hours after the peak flow even through flow events may last longer or shorter than this.

3.3 Statistical analysis

Analysis of variance (ANOVA) was used in two separate ways to assess the impact that drain blocking had upon both the DOC concentration and DOC flux. Firstly, the DOC concentration change from the every single events was considered along with the factors: year, month, site, scale, and blocking statue. The Month factor has 12 levels, one for each month of the year. The site had 6 levels one for each of the monitored catchments. The scale factor had two levels, zero and first order. Even through the site differences would explain more variance of data set, the scale factor was included in this analysis to minimize the difference of the actual site difference. The blocking had two levels: blocked and unblocked. Along with the four main factors, the hydrological data including: rainfall total, rainfall duration, peak rainfall intensity, flow lag time, peak flow, antecedent flow, and time between events were used as covariates. The same analysis was repeated for change in the DOC flux.

To negate effects of the natural variations in DOC from year to year, both the DOC concentration change and DOC flux changes of a blocked drain in experimental catchment were considered relative to the DOC concentration and DOC flux of an unblocked drain of the same scale in the control catchment at the same time. Relative DOC was calculated by the ratio of the monthly average DOC concentration or DOC flux of a blocked and unblocked drain from the experimental and control catchments respectively. The relative DOC concentration and flux changes were subject to ANOVA as above.

The event analysis included a large range of hydroclimatic characteristics and responses and therefore a multivariate analysis was required to produce easily interpretable results. Principal components analysis (PCA) is a multivariate analysis that allows data described by multiple primary variables to be converted into the same number of principal components, which are mutually orthogonal (Harrington et al., 2005). The principal components combine variables from the original dataset and are calculated in the order of decreasing proportion of the original variance explained. In doing so it is hoped that by using PCA the number of components which need to be examined is fewer than the original number of variables while also highlighting multiple associations and correlations between the original set of variables. Therefore, PCA was employed here to look through the impact of hydrological factors on DOC concentration and DOC flux of the flow events.

The variables used in PCA were: rainfall total (mm), rainfall duration (hour), peak rainfall intensity (mm/hour), flow lag time (hour), peak flow (m^3/s), antecedent flow (m^3/s), and time between events (hour). The PCA was first performed with DOC concentration and then applied to DOC flux. Because the variables have different units all data were converted to standard normal distribution by using z-transform before analysis. The z-transform is:

$$Z = \frac{(X-\mu)}{\sigma} \qquad \text{eq. 3.1}$$

Where: x is a raw value 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.

To assess which of the principal components (PC) would be retained for assessment the following rule was applied: Chatfield and Collins (1980) states that when analyzing a correlation matrix from a PCA the sum of the eigenvalue is equal to the number of variables, therefore components with eigenvalues less than 1 may be disregarded as they represent less variance in the original data than a single variable. Therefore, in the events analysis here, all PCs with eigenvalues greater than 1 were considered but the first PC with eigenvalue less than 1 was also included.

Christophersen and Hooper (1992) discussed multi-end-member interpretation in combination with principal components analysis to identify the source solutions from potential groundwater mixtures. The end-member mixing approach was then widely used as an efficient analysis to evaluate the ability of independently measured source compositions of combined water sources (Worrall et. al., 2003). Christophersen and Hooper (1992) argued that PCA can only be used to identify the number of end-members prior to using the EMMA approach, however, Worrall et al. (2003) argued this assumption is only valid if the end-members are independently measured. However, the PCA doesn't presume the nature of the end-members and the EMMA is dependent on the end-member composition and its antecedent conditions (Soulsby et al., 1995). In this study the composition at the catchment outlet and the antecedent characters such as antecedent rainfall and antecedent flow (see illustration in Figure 3.1) are gathered over the same time period with the same frequency. This means the end-member mixing analysis can be performed for each component and in combination to understand the sources and controls on the composition of the events. Furthermore, the scores on key principal components (PCs) were chosen for ANOVA. This process is aimed to investigate if these PCs are significant influenced by the blocking. During the ANOVA, scale, blocking status, and month were considered as the factors, whereas DOC flux was considered as a covariate. The factors had the same levels as described above.

3.4. Result of DOC Concentration

During the three years of study, there were 2710 rainfall events recorded from six drains. Among these 2710 events, there were 1626 rainfall events which could be matched with a measurable flow event and 1080 events with no identical flow events. That means there were 271 days out of three years which were under the peak flow conditions. However, equipment problems meant that the automatic sampler only collected samples every 24 hours, therefore when DOC concentration or export were considered then only 756 out of 1626 events could be included for analysis. A detailed description of the analyzed rainfall and flow events can be found in Table 3.1.

Descriptor	control		Experimental	
	max	min	max	min
Total Rainfall (mm)	33.6	0.2	33.6	0.2
Rainfall durations (h)	28.8	0.2	28.8	0.2
Rainfall intensity (mm/h)	25.6	0.08	25.6	0.08
Flow lag time (h)	3	0.25	3	0.25
Peak flow (m3/s)	0.430733	1.12×10^{-8}	0.700052	3.07×10^{-7}
Antecedent flow (m3/s)	0.430733	1.12×10^{-8}	0.700052	3.07×10^{-7}

Table 3.1: Detailed description of recorded rainfall and flow events.

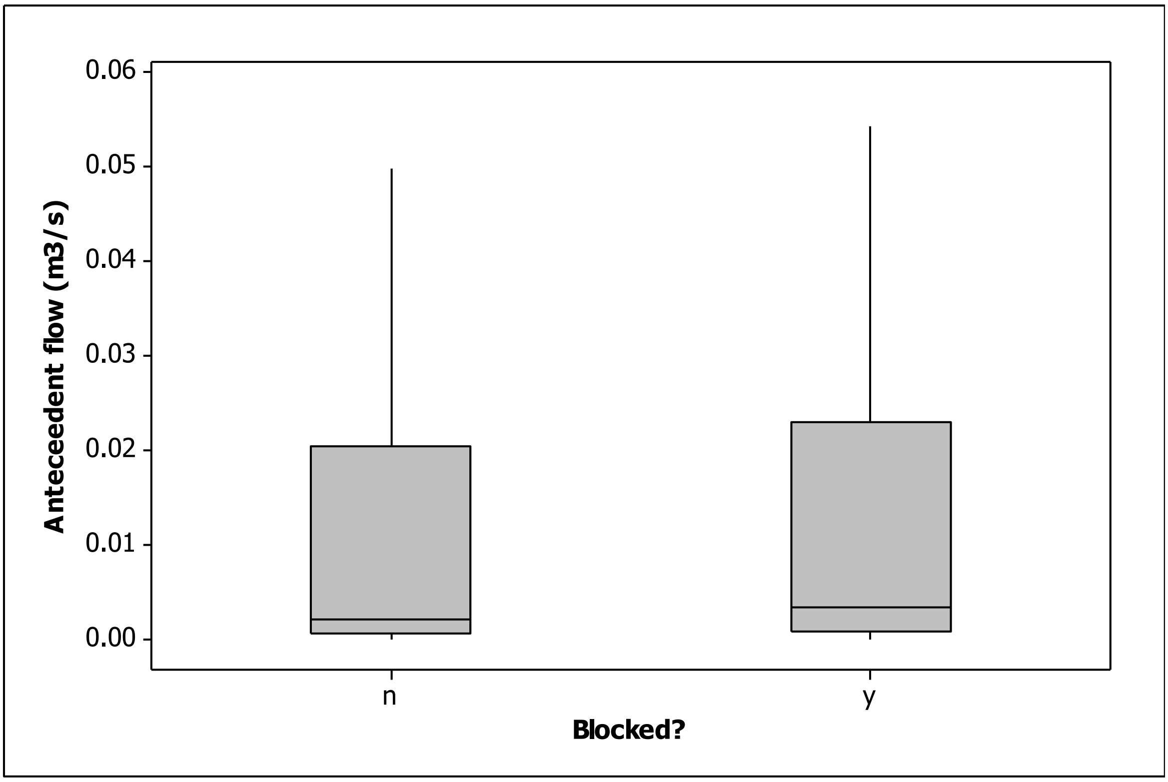

Figure 3.2: Box plots of antecedent flow of blocked and unblocked drains. The lower whiskers (low 25% of data) of blocked drain in both scales are too close to up boundary of interquartile box to shown in figure.

The antecedent flow as an estimated base flow of the events, showed no significant change before and after blocking (Figure 3.2), however flow lag times were observed to increase after blocking (Figure 3.4). The flow lag times could be influenced by the different factors, i.e. scale of drains and the different slope of the catchments. Most likely the different flow lag time could be controlled by combined effects of different variances. A series of ANOVA were applied on antecedent flow, peak flow and flow lag time. Table 3.2 shows an ANOVA for antecedent flow. Factors included in the analysis of antecedent flow are blocking and scale. Results found only scale as a significant factor, which explained 18.5% of data variance. As shown in Figure 3.2, no impacts of blocking were received by antecedent flow. The peak flow events in drains (Figure 3.3) significantly increased after blocking. Table 3.3 shows results of the ANOVA for peak flow using scale of drain, and blocking as factor and antecedent flow as covariate. Both factor and covariate were found significant in Table 3.3 where antecedent flow explained 67% variances, blocked explained 0.41% variances and scale explained 1.47% of variance. Among all three factors and the covariate in Table 3.3, antecedent flow was found the most influential factor which alters event peak flow, where scale and blocked had less impact towards the variances of peak flow compare to antecedent flow. Table 3.4 shows an ANOVA of the flow lag time changes.

Source	DF	P	Portions of variances
Scale	1	<0.001	18.50%
Error	754		
Total	755		
R-Sq = 18.67%			

Table 3.2: Results of ANOVA for antecedent flow.

The factors used in this ANOVA for flow lag time are blocking status (Blocked/ Not blocked), and scale of drains (Zero scale/ First scale). Besides the two factors, antecedent flow and rainfall intensity were included in the ANOVA as covariates. The ANOVA of flow lag time found blocking as most important factor by which explained 17.4 % of variance. Scale didn't show any significance in the analysis. Both the covariates were found as significant factor with respect of explaining 4.35% of data variances by antecedent flow and 2.85% variances of data by rain intensity. Changes of the events parameters may effects water runoff reaction to the flow events after blocking been applied i.e. the increase of flow lag time after blocking would in turn enhance the stream runoff.

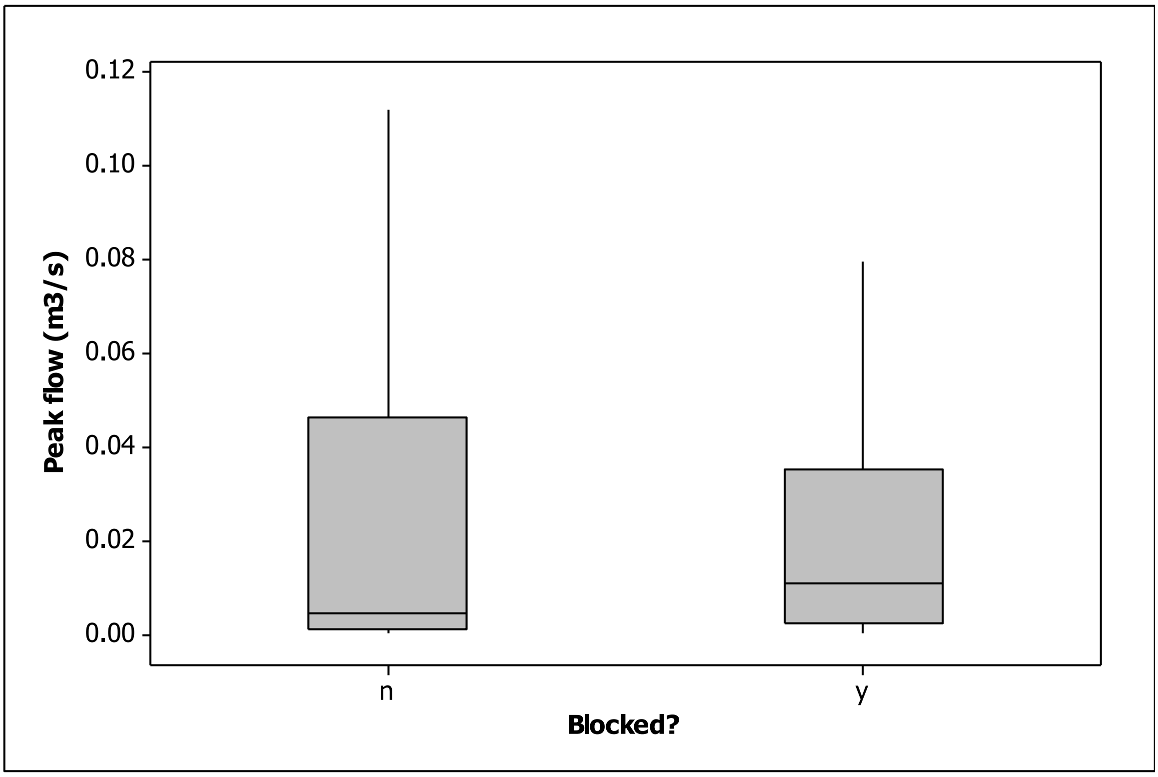

Figure 3.3: plots for peak flow and antecedent flow measured from drains, prior and after blocking. The lower whiskers (low 25% of data) of blocked drain in both scales are too close to up boundary of interquartile box to shown in figure.

Antecedent flow	1	<0.001	66.96%
Blocked?	1	<0.001	0.41%
Scale	1	<0.001	1.74%
Error	752		
Total	755		
R-Sq = 69.27%			

Table 3.3: Results of ANOVA for peak flow.

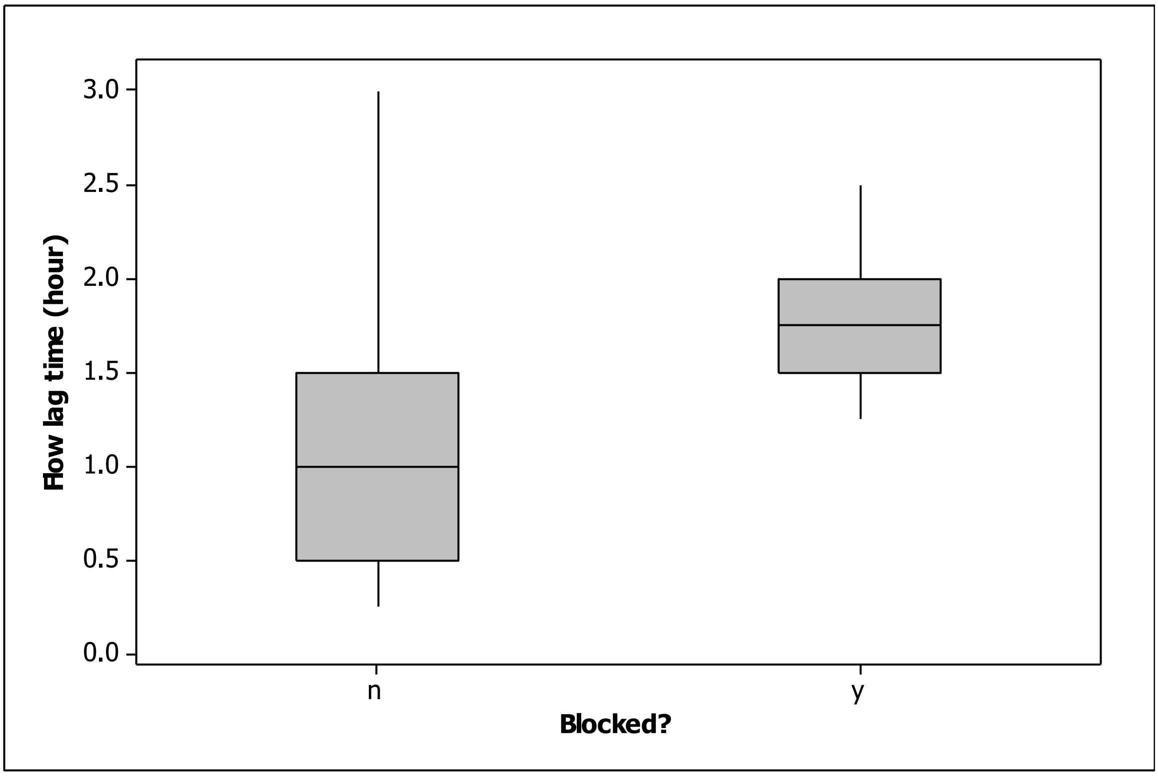

Figure 3.4: plots for flow lag time measured from drains, prior and after blocking.

Source	DF	P	Portions of variances
Rain Intensity (mm/hour)	1	0.001	2.86%
Antecedent flow	1	<0.001	4.35%
Blocked?	1	<0.001	17.24%
Error	435		
Total	438		
R-Sq = 25.01%			

Table 3.4: Results of ANOVA for Flow lag time.

3.4.1. DOC concentration

The DOC concentration has been calculated on a total of 5960 samples. Of these water samples only 756 could be associated with the flow events. Analysis of variance (ANOVA) was performed on the DOC concentration data from Cronkley and covariates from the next day hydrological behavior. In the ANOVA of 756 DOC concentration, the data set of DOC concentration was replaced by its logged value so as to give a normal distribution (For details of ANOVA see chapter 2). The following factors of ANOVA of DOC concentration changes of events were found to be significant: month, site, and blocking status. The combination of covariates and factors explained 50.78% of the original variance. Site was the most important factor and explained 42.52% of the original variance in the dataset. The month and blocking factors explained 4.2% and 3.29% of the original variance respectively.

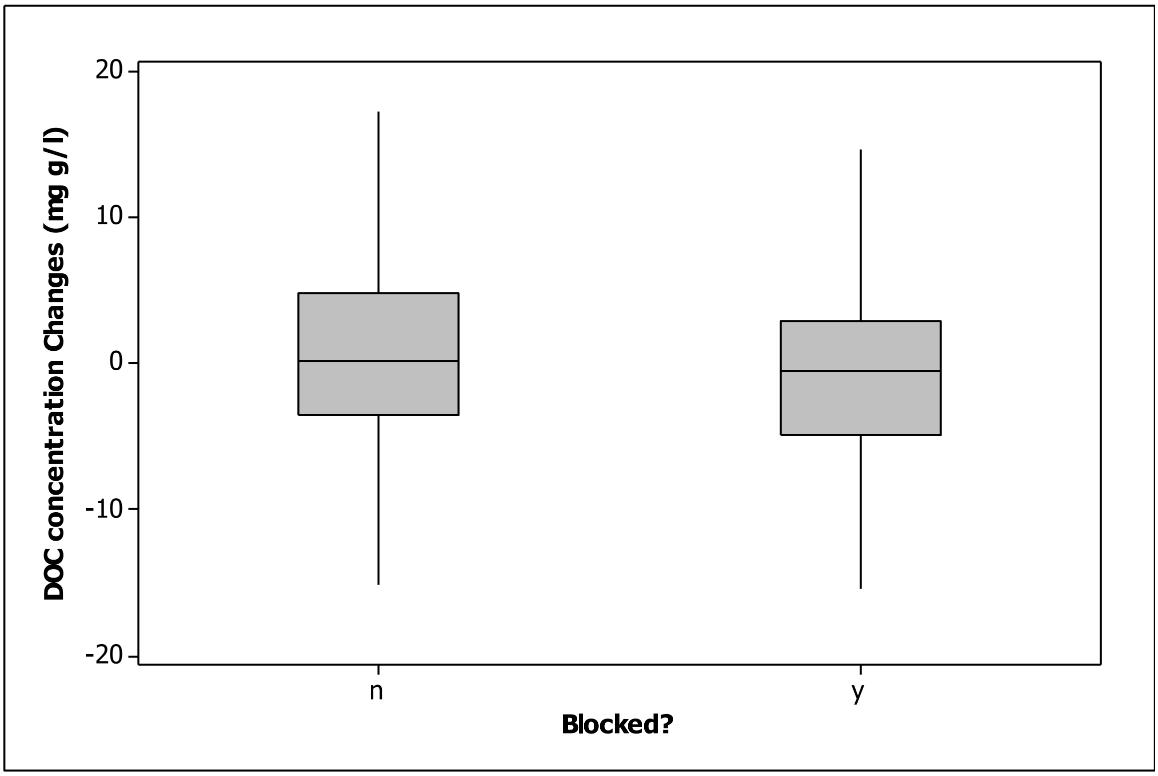

Figure 3.5: DOC concentration changes before and after blocking.

The site and scale factors are correlated and so when the scale was used as a factor instead of site, it was found that flow lag time, month, scale, blocking statue were significant and explained 31.99% of variance. In this case scale was the most important factor and blocking still only explained a small portion of the original variance (0.94%). The significant effect of blocking was an average a decrease in DOC concentration changes of 0.8 mg g/l (Figure 3.5), i.e. the change in DOC concentration across an event was smaller after blocking.

A clear difference between zero and first order drains can be observed for the control catchments (Figure 3.6). The decrease in DOC concentration changes can be ascribed to the greater dilution potential at scale and the longer residence time leading to greater DOC losses via degradation processes.

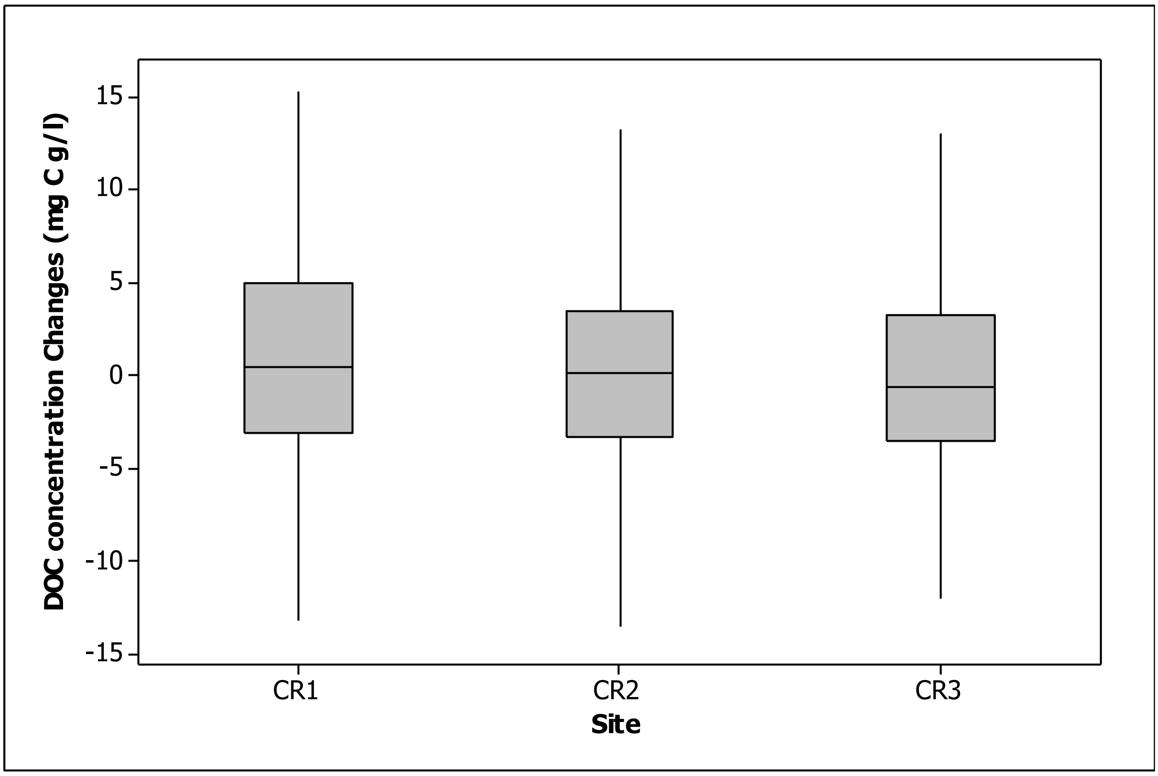

Figure 3.6: DOC concentration changes in control catchment (where CR1 and CR2 are zero order drain and CR3 is first order drain).

The whisker plots of the experimental catchments show a similar pattern between the DOC concentration changes between the different scales as observed for the control catchments (Figure 3.7), where the zero order drains (CR5, CR6) show lower DOC concentration changes than the first order drain (CR4) before blocking. Among two zero order drains, CR6 showed relative smaller changes compare with CR4 and CR5 before and after blocking, while CR5 showed a decrease after blocking. The different DOC concentration changes could be due to a number of reasons, however the most likely is that different setting of experimental catchment compared to the control catchment: unlike the control catchment both zero order drains in the experimental catchment can be seen as two parallel bypass drains to the first order drain, only CR6 can be seen as such a bypass drain in the control catchment, CR5 is independent of CR4 (first order drain) and linked directly to a shake hole. In this case, the significant decrease in DOC concentration changes after blocking observed in CR4 can be explained by a combination of DOC concentration changes by itself and an accumulation of DOC concentration changes from both CR6 and CR4. Vice versa, because the independence of CR5 to CR4, therefore DOC concentration changes of CR5 were not affected by the DOC concentration changes of CR4. Another possible reason of the bigger DOC concentration changes in first order drains after blocking is that the bigger scale drain might receive more influence from the blocking than smaller scale drains in the experimental catchment. Blocking may have caused changes in flowpath during events that caused water to go deeper into the soil and flush out higher DOC concentration soil water. As mentioned earlier, the flow lag time is only dependent upon the blocking rather than upon scale. After blocking both scales of drain would have had longer flow lag time that triggered the events water exchanges with deeper soil water.

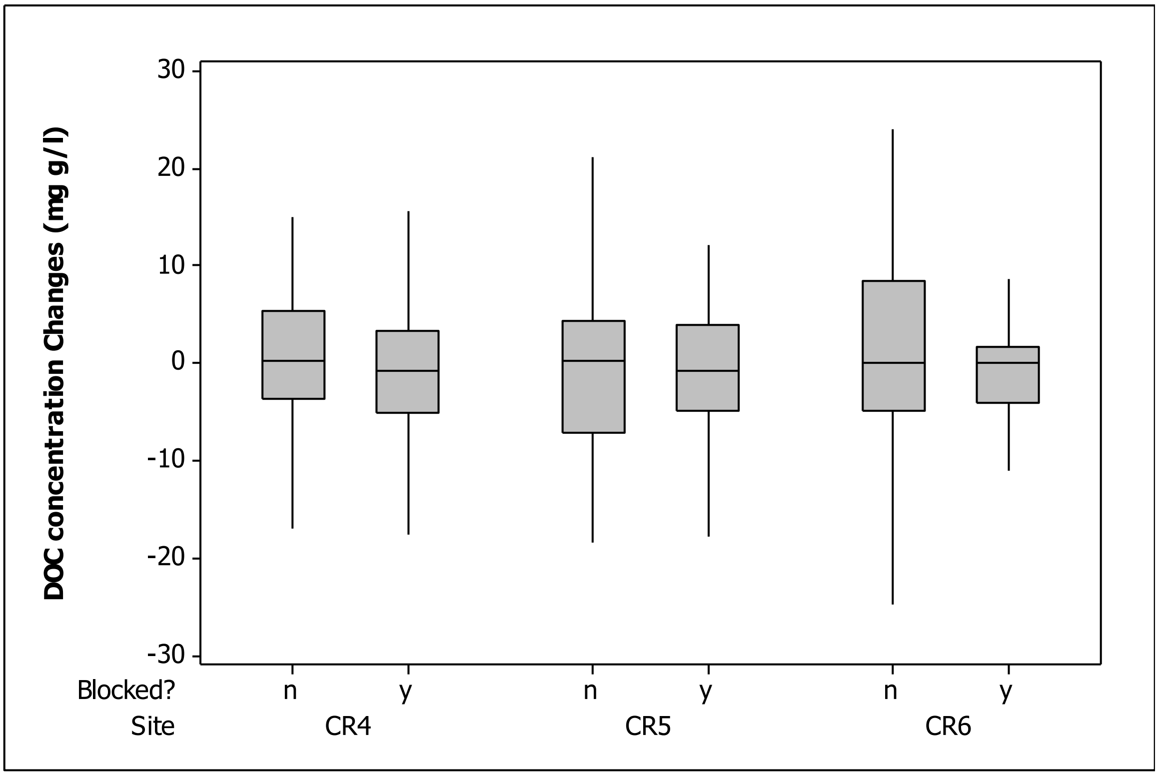

Figure 3.7: DOC concentration changes in experimental catchment.

As the first order drain is bigger than the zero order drain, there would be more high DOC concentration deeper soil water exported from depth in the soil, which resulted in the greater decrease in the DOC concentration change across events for the larger scale drains after blocking.

3.4.2 Relative DOC concentration

The comparison of the relative DOC concentration on both zero and first order drains (Figure 3.8) shows the same trends at the different scales as observed above. In the zero order drains, relative DOC concentration change decreased by 54.5% after blocking. On the other hand, first order drains (Figure 3.7) showed a dramatic decrease in relative DOC concentration change after blocking (94.1%). The different relative DOC concentration change between zero and first order drains might be for various reasons. As observed on DOC concentration changes, DOC concentration changes increase with scale.

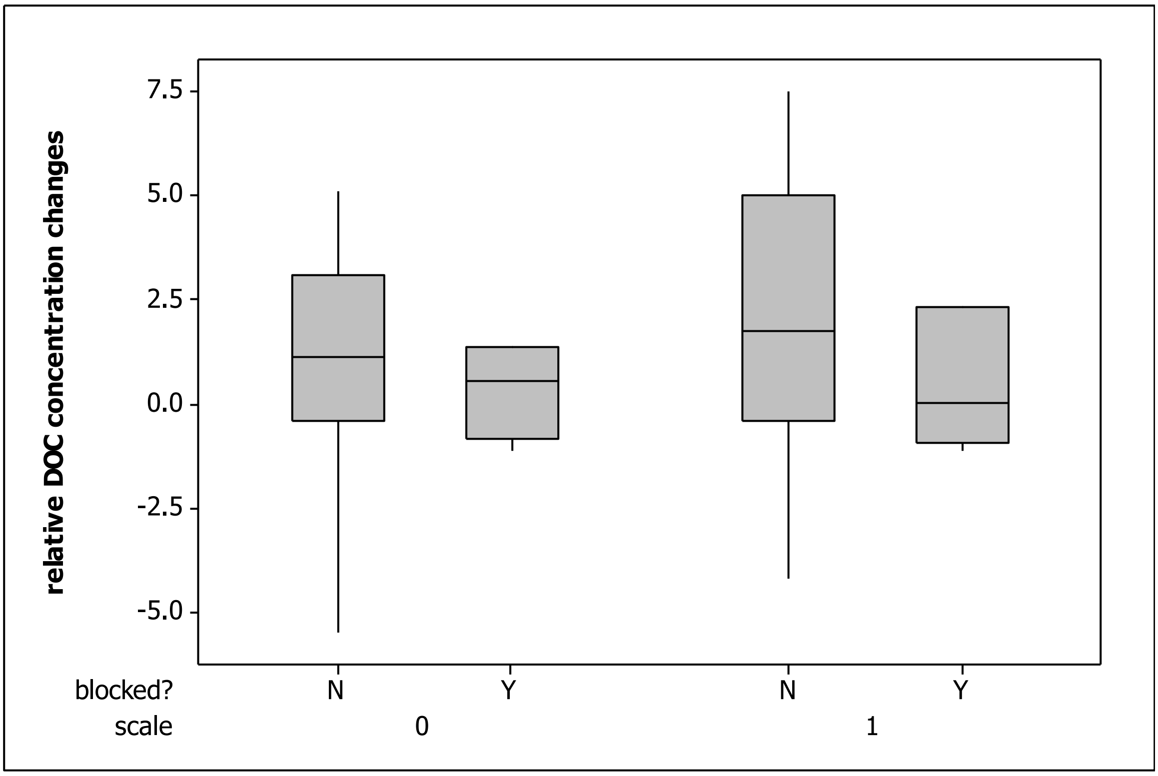

Figure 3.8: Relative DOC concentration changes before and after blocking in both scales. The upper whiskers (top 25% of data) of blocked drain in both scales are too close to upper boundary of interquartile box to be visible in the figure, which duo to the lower available samples in blocked drains compare to unblocked drains.

Brown et al. (1999) indicate that for intense rainfall events, the events contribution to peak runoff decreases with the increase catchment size. The events analysis conducted here is on selection of the high peak flow events with relative high rainfall totals, therefore, it is likely to suit the situation Brown et al. described. On the other hand, Brown et al .(1999) linked the catchment size effects with the changes of flowpath, in which the pre-event ground water was involved and they indicated a downstream increase in groundwater compared to storm water. The greatest contribution of event water to storm flow was in the smallest catchments where the near stream ground water reservoir was probably smaller. Therefore, the higher order drain is more likely to see a dilution effect from the ground water. The blocking of the higher order drain increases the flow lag time of the event, which would lead to the mix of event water and pre event flow, this dilution impact would have a much bigger impacts on bigger scale drains. The PCAs of the hydrological data and end-member analysis of the different chemical tracers of the stream water were used to further investigate this difference.

3.5. Principal components analysis of DOC Concentration

Four PCs were selected based upon the rule that eigenvalues > 1 and the first < 1, and together they explained 76% of the original variance. Table 3.5 shows the loadings on the PCs and that rainfall total, rainfall duration, time between events, flow lag time were all unrelated to DOC concentration changes across all PCs. Traditionally, loadings of approximately 0.5 were selected as important, however the analysis performed here considered loadings bigger than 0.4 as important to include more possible variables. The considered important loadings have been highlighted as red on the Table 2 – it should be noted that there is no statistically-based rule that allows one to identify variables of importance within a PC. The first two components together explained 48.2% of dataset variance and PC1 represented 26.3% of the data variance. Normally, the first component

(PC1) is interpreted as a measure of overall variances and facilitates normalization of the data variances (Worrall et al., 2003). In this events analysis, the z score standardized the

Variable	PC1	PC2	PC3	PC4
Z Rainfall Total (mm)_	0.517	0.447	-0.052	-0.031
Z Rainfall Duration (hours)_	0.524	0.426	0.120	-0.050
Z Rainfall Intensity (mm/hour)_	-0.057	0.079	-0.750	0.018
Z Flow lag time	0.220	-0.193	0.547	0.106
Z Antecedent flow	0.411	-0.532	-0.129	-0.008
Z Peak flow	0.392	-0.534	-0.166	-0.133
Z Time between events	-0.289	-0.075	0.276	-0.162
Z DOC concentration changes	-0.029	0.034	0.019	-0.970
Eigenvalue	2.1077	1.7514	1.1592	1.0128
Proportion	0.263	0.219	0.145	0.127
Cumulative	0.263	0.482	0.627	0.754

Table 3.5: Hydrological loadings of first four PCs.
Absolute loading values bigger than 0.400 were considered as dominant loadings and marked red.

variables prior to the PCA, therefore PC1 here represents the actual changes in variables rather than the difference between units.

In the four PCs, both PC1 and PC2 are mainly governed by changes in: rainfall total, rainfall durations, peak flow, and antecedent flow. However, PC1 increases with all four of these variables, while PC2 only increases with increased rainfall total and rainfall duration but increased with decreasing peak flow and antecedent flow. PC1 seems to distribute effects of the rainfall to the flow, i.e. increases in rainfall and increased antecedent flow lead to increased peak flow. On the other hand, the PC2 shows negative loadings of antecedent flow, peak flow and positive loading of rainfall total and rainfall duration. In this case, even though the total rainfall and rain durations were getting bigger, the peak flow was still decreasing. The decreased peak flow here might simply be due to the decreased antecedent flow. Other possibilities include that this PC represents rainfall event which with high rainfall total, high rainfall duration but low rainfall intensities, and therefore, peak flow could be low during such long rainfall periods. Besides the above hypothesizes, Holden et al. (2008) pointed out the existence of the peat pipes, which are common features of peat land (Holden et al., 2002) may provide the event water with an additional flow path through the sub soil that leads to the decreasing of the peak flow. The hypotheses given here maybe PC2 may represent a combination of potential flow path effects and low rain intensity effects upon the peak flow. Therefore, PC2 here is used as an interpretation of counter factor besides PC1 which represent the effects of rainfall.

The PC2, PC3 are dominated by positive loadings for flow lag time and negative loadings of rainfall intensity. Loadings of PC3 suggest relationship between decreasing rain intensity and increasing flow lag time. Loadings of PC4 show negative loadings of DOC concentration changes, which make PC4 represent the factor of the DOC concentration changes during the events.

Four individual components were divided to several groups to test the relationship between hydrological factors and DOC concentration changes during the events. PC1 and PC2 were first grouped together as both them shared the same important loadings through each of them represent different movement of the event water. PC3 is then joined separately to PC1 and PC2 as PC3 illustrate a periods of time between events that may show different influences on different event water movements. Lastly, PC4 was considered with PC1 and with PC2 to test the DOC concentration changes on two types of event water movement. The above tests were presented separately on control and experimental catchments so as to highlight the differences before and after blocking on the study catchments.

3.5.1. Comparison of PCs on control catchment

Comparing PC1 and PC2 (Figure 3.9) shows that there is no major variation caused by DOC concentration changes in the first two components but rather an interaction between the hydrological changes.

Four end-members have been identified (Figure 3.9 - A, B, C, D). End-member A produces the lowest score on the PC1; end-member B gives the highest datum on PC2; end-member C is the lowest score plot on PC2, and end-member D is the highest score plot on PC1. The score plots (Figure 3.9) show two major trends which are almost perpendicular to each other. These two trends are separated by the differences in the scales of the drains. Among both scales, trend line AB mainly contains the score plots from zero order drains while trend line AC covers the majority of the score plots from first order drains. The detail of four individual end-members may illustrate the hints of the transitions between AB and CD (Table 3.6). End-member B and D happen to represent the same day, thus the difference of this two end-members give a clear demonstration of the difference between trend line AB and CD. As both end-members B and D have the same rainfall duration and rainfall total and rain intensity the differences that separated them apart are the different flow lag time, peak flow and antecedent flow. The further comparisons between group AB and CD shows the shift between first order and zero order drains were mainly happened on the PC2 axis. PC1 is controlled by the positive loadings of total rainfall, rain duration, peak flow and antecedent flow. As mentioned earlier PC1 represents a hydrological relationship that the flow would increase with increasing rainfall. Therefore, end-member A represents the events that have low flow conditions and low rainfalls. From Table 1, PC2 represents the condition that as rain fall increases, the antecedent flow and peak flow are still decreasing. This may suggest that the base flow is not dependent on the current rainfall. Thus, end-member B shows the events with the low peak flow and antecedent flow but with the high rainfall total and rain duration.

The Line AB shows that the zero order drains were controlled by the events under the increasing rainfall, low peak flow with low antecedent flow. On the contrary, end-member C has the lowest score on PC 2 which has negative loading of peak flow, antecedent flow and positive loadings of rainfall total and rainfall duration. Therefore, trend line AC shows that major transition between zero order to first order drain, however all the loadings were increased from A to C. End-members B and D are easier to compare in this situation as they sharing the same rainfall total and rainfall duration. Noticeable, the changes between B and D were mainly by different flow lag time.

End-member	Date	Site	Scale	RT	RD	RI	FLT	PF	AntF
A	28/03/2008	CR1	0	0.2	0.2	1	1	0.0005	0.0005
B	04/08/2008	CR1	0	28.8	28.8	1	1.25	0.0005	0.0004
C	10/11/2008	CR3	1	0.6	0.25	2.4	2	0.3945	0.2672
D	04/08/2008	CR3	1	28.8	28.8	1	2	0.3247	0.2499

Table 3.6: Hydrological characters of the four end-members in control catchment.
Where RT: Rainfall total (mm); RD: Rain duration (hour); RI: Rain intensity (mm/hour); FLT: Flow lag time (hour); PF: Peak flow (m^3/s), AntF: Antecedent flow (m^3/s).

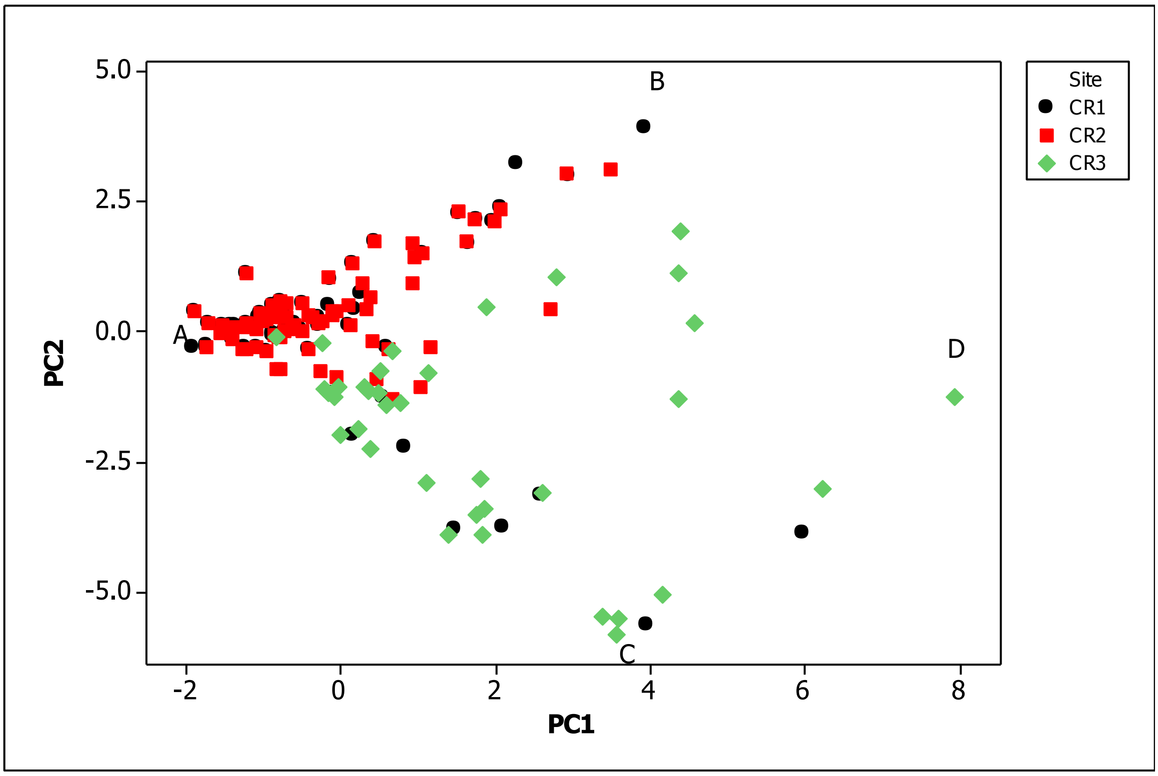

Figure 3.9: Score plot PC1 vs PC2 on control catchment.

The difference between the two scales of drains is the different flow lag times: this may indicate that there are other factors controlling the event flow rather than the ones included in this PCA.

The same separation can be observed on the plots that PC2 against PC3 (Figure 3.10). As mentioned before that PC2 is general interpreted as representative of influence of high rainfall but low rainfall intensity events. PC3 is taken to represent time periods which the time between events was getting longer and rain intensity was decreasing. In Figure 3.10, there is a clear separation between zero order drains and first order drains on the axis of PC2. In control catchment, majority of the events plot on the positive end of PC3. In other words, during the long flow lag time and low rain intensity events periods, zero order drains reflect more events with small peak flow and antecedent flow under bigger rainfall total and rainfall duration; first order drain have the events with smaller rainfall total and rainfall duration but bigger peak flow and antecedent flow. On Figure 3.10, two end-members were identified. These two end-member represent the same day of the hydrological events C and B in Figure 3.9. Their hydrological details were given by Table 3.7. In Table 3.7, it is clear that the rise and fall of event flow were following the same trend of rainfall intensity and flow lag time. When the flow lag time were decreased from C to B, peak flow and antecedent flow also decreased despite that end-member B has bigger rainfall total and rain durations. It is noticeable that in end-member C, the rainfall duration is much smaller than flow lag time which means that by the time the rainfall stops, the steam is still receiving event water.

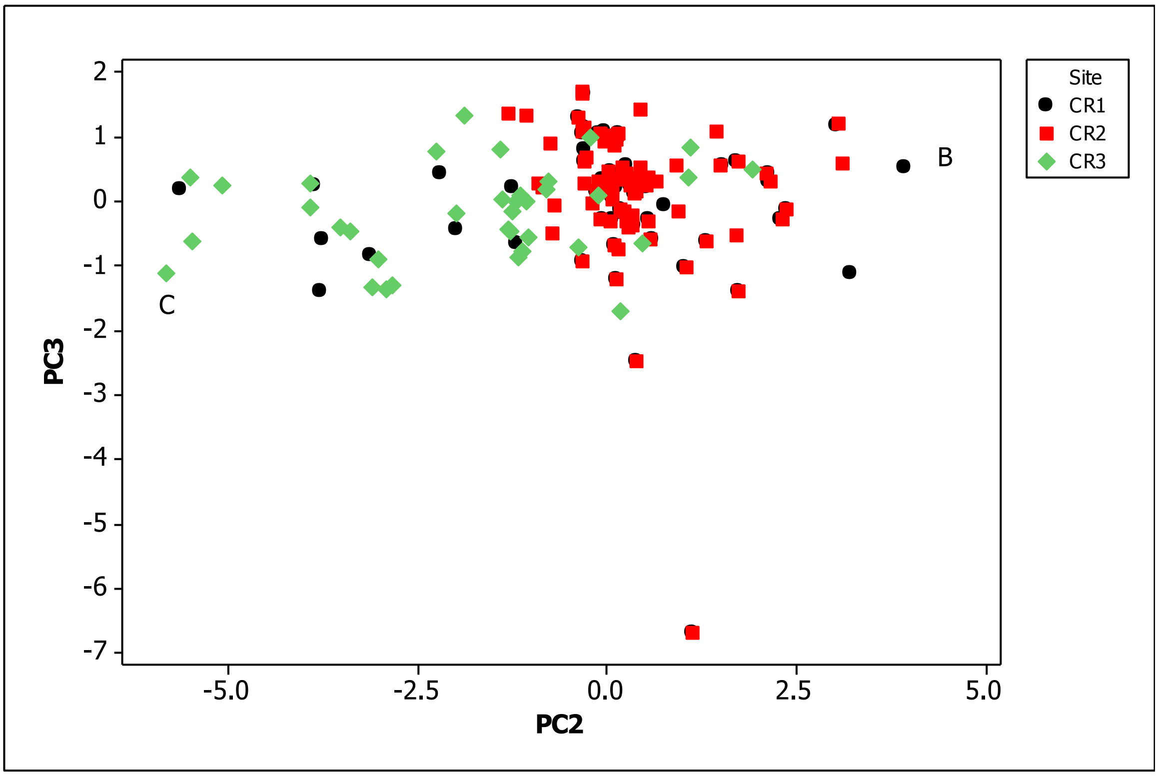

Figure 3.10: Score plot PC2 vs PC3 on control catchment.

End-member	Date	Site	Scale	RT	RD	RI	FLT	PF	AntF
C	10/11/2008	CR3	1	0.60	0.25	2.4	2.00	0.3445	0.2672
B	04/08/2008	CR1	0	28.8	28.8	1.0	1.25	0.0005	0.0004

Table 3.7: Hydrological characters of the two end-members In control catchment.
RT: Rainfall total (mm); RD: Rain duration (hour); RI: Rain intensity (mm/hour); FLT: Flow lag time (hour); PF: Peak flow (m3/s), AntF: Antecedent flow (m3/s)

It could be the situation, as shown in end-member C, that it is during the short time of periods with high intensity rainfall that leads to the flushing of the drain and creates high peak flow. On the other side, end-member B has the longer rainfall duration compared to flow lag time, which means the stream is receiving event water, and therefore event flow should increase. But the low intensity rainfall stretched over a long period of time leads to actual smaller peak flow events. The low rain fall intensity may not be the only reason that caused the observed low peak flow in end-member B. As stated before the long rainfall duration with low rainfall intensity gives more chances that events water may drain through other flowpathes i.e. peat pipes. In addition to the hydrological differences of end-member C and B, the two end-members also represent two different scales of drain. Event water in the smaller scale drain would eventually go to the bigger scale drain. Therefore, the impact of the rainfall events, i.e. the increase of the peak flow would more likely to be accelerated to the bigger drains.

When PC1 was plotted against PC3 (Figure 3.11), contributions of peak flow and antecedent flow was increased with increasing rainfall total and rainfall intensity. The clear separation in Figure 3.10 is less noticeable, and the higher order drains were dominated by high rainfall, high flow events while the lower order drain caught more low rainfall low

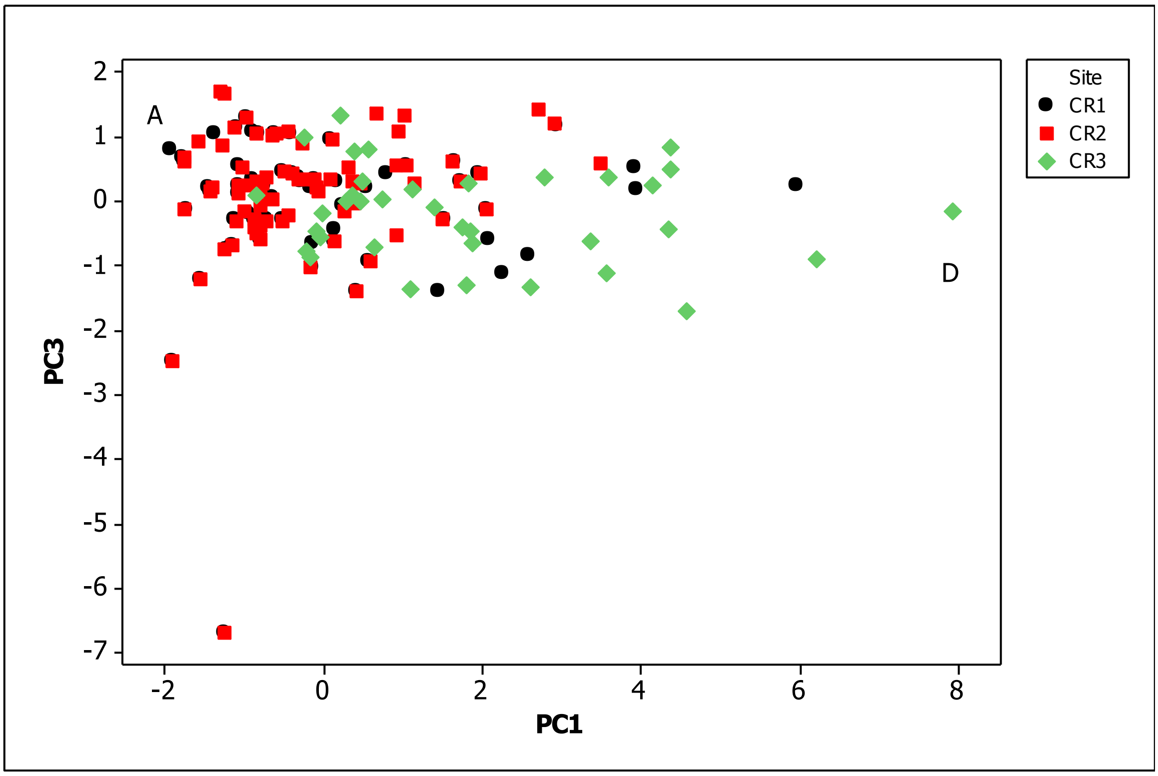

Figure 3.11: Score plot PC1 vs PC3 on control catchment.

flow events. A possible explanation in PC2 vs PC3 is that the event flow is more dependent on the rain intensity and flow lag time. End-member analysis was applied to a graph of PC1 vs. PC3. Two end-members were identified A and D, the same as in Figure 3.10 (the two end-member are the same events A and D as identified in Figure 3.9). Comparison of two end-members showed that the lower order drains reflects more changes under smaller rainfall total, rainfall duration events and also smaller peak flow events. On the contrary, the higher order drain represents bigger rainfall duration, rainfall total and high peak flow events. Table 3.8 gives the details of the two end-members. End-members A and D represent events with same rainfall intensity albeit the end-member D has bigger flow lag time than end-member A, the rainfall durations clearly play a far more important role in controlling the peak flow here. The same scale differences that lead to separation of events in Figure 3.10 were also featured in Figure 3.11. Rainfall character has a greater influence on first order drains than on zero order drains.

End-member	Date	Site	Scale	RT	RD	RI	FLT	PF	AntF
A	28/03/2008	CR1	0	0.20	0.20	1	1	0.0005	0.0005
D	04/08/2008	CR3	1	28.8	28.8	1	2	0.3247	0.2499

Table 3.8: Hydrological characters of the two end-members In control catchment.*RT: Rainfall total (mm); RD: Rain duration (hour); RI: Rain intensity (mm/hour); FLT: Flow lag time (hour); PF: Peak flow (m^3/s), AntF: Antecedent flow (m^3/s).*

The comparison between first three PCs gives an insight into the hydrological changes in the control catchment during the study period. Of the all the principal components PC4 is the only principal component that demonstrates a dominant loading for the DOC concentration changes among all four principal components. The comparisons between PC4 and PC1; and between PC4 and PC2 were therefore plotted to demonstrate patterns of DOC concentration in the control catchment. PC1 and PC2 are selected because they represent the two kinds of rainfall event as interpreted earlier: a high rainfall total, high rainfall duration with high rainfall intensity event; and a high rainfall total, high rainfall duration but low rainfall intensity event.

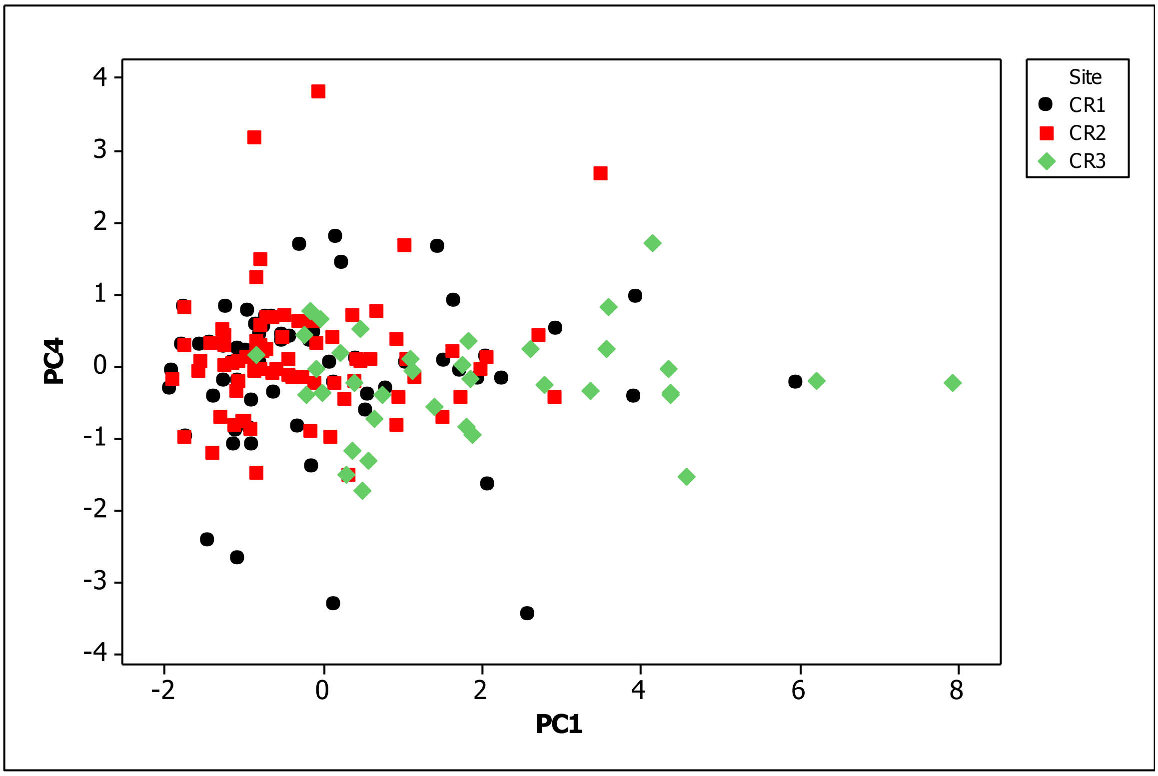

Figure 3.12: Score plot PC1 vs PC4 on control catchment.

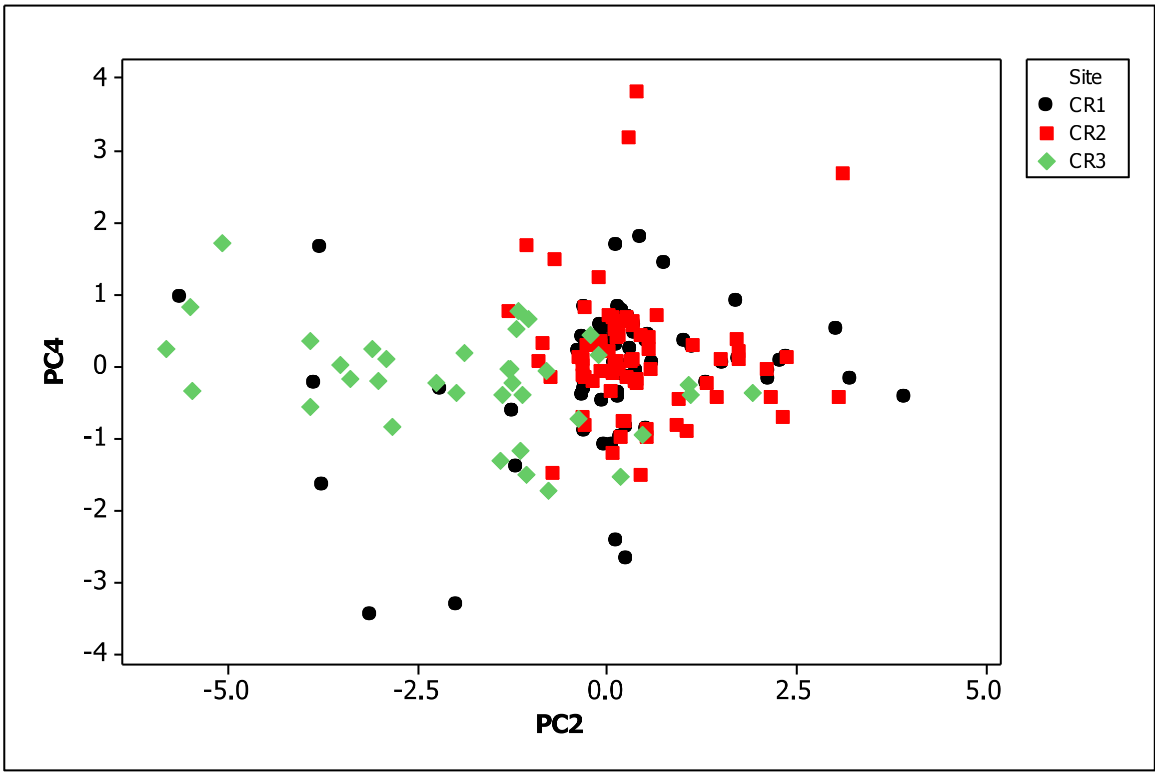

Figure 3.13: Score plot PC2 vs PC4 on control catchment.

In the scatterplots of PC1 vs PC4 and PC2 vs PC4 (Figures 3.12 and 3.13), there are no clear DOC concentration changes on the PC4 axis that divide between the scales or between the event types identified.

The scatterplot of PC3 against PC4 (Figure 3.14) is gathered by plots that are patterned around zero axis. There are no DOC concentration changes that been altered by the PC3 which stand for the increasing flow lag time but decreasing rainfall intensity.

The PCA of the flow event here demonstrated two different kinds of rainfall events that have different impacts on the peak event flow of the control catchment. However, the analysis failed to clearly illustrate how the DOC concentration changes between the catchments.

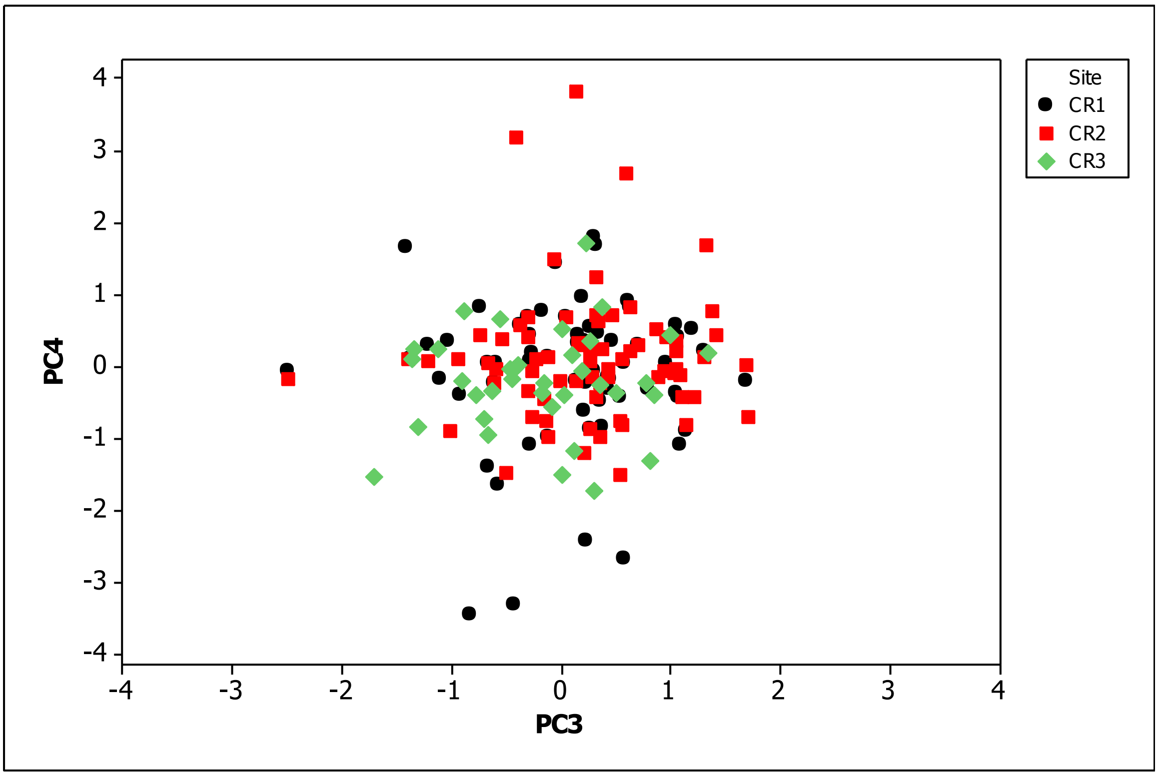

Figure 3.14: Score plot PC3 vs PC4 on control catchment

3.5.2. Comparison of PCs on the experimental catchments

In the experimental catchments four end-members E, F, G, H, were selected. End-member E has the lowest scores on PC1. End-member F has the highest score on PC2. End-member G has the lowest score on PC2, while end-member H has the highest score on PC1. Details of the four end-members are given in Table 5. These four end-member events were all from the non- blocking periods. Score plots of PC1 against PC2 (Figure 3.15) shows the trend EF and GH, where events from both the zero order and first order drains plot. Figure 3.15 shows a similar but suppressed pattern compared to Figure 3.9. In Figure 3.15, there are three parallel lines which divided roughly by each drains that move from E (G) end to F (H) end. The separation between two different scales of drains observed for the control catchments (Figure 3.9) still exists, but the boundaries between the drains of different scales start over lapping on each other in the experimental catchment.

End-member	Date	Site	Scale	RT	RD	RI	FLT	PF	AntF
E	06/05/2008	CR6	0	0.2	0.2	1	0.25	0.004	0.004
F	04/08/2008	CR6	0	28.8	28.8	1	1.25	0.003	0.002
G	03/05/2008	CR4	1	1	1	1	0.5	0.198	0.075
H	04/08/2008	CR4	1	28.8	28.8	1	2	0.046	0.043

Table 3.9: Hydrological characters of the four end-members in experimental catchment
RT: Rainfall total (mm); RD: Rain duration (hour); RI: Rain intensity (mm/hour); FLT: Flow lag time (hour); PF: Peak flow (m^3/s), AntF: Antecedent flow (m^3/s)

In the control catchment, there was clear evidence that PC2 represented low intensity rainfall events. However, in Figure 3.15 there are no differences in rainfall intensity between

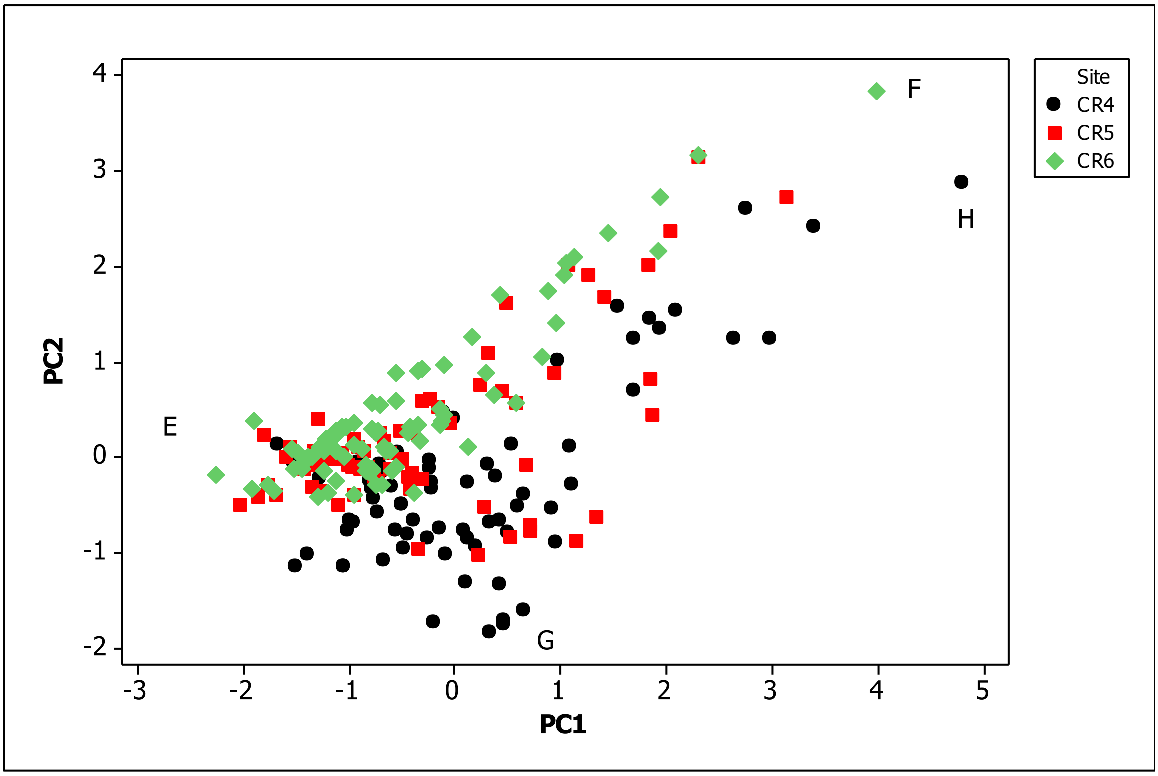

Figure 3.15: Score plot PC1 vs PC2 on experimental catchment

the two extreme end-members F, G, on the experimental catchment (Table 3.9). Hence, there should be other features that explained the variation along PC2 on the experimental catchments. A further study of the hydrological characters of the four end-members reveals that all four end-members have the same rainfall intensity despite different rainfall total and rainfall durations. The events from the first order scale drains still show that they have a greater peak flow during the flow events.

End-member E still has the longer flow lag time than rainfall duration, which could explain its low peak flow. However, the comparison of two trends, EF and GH, reveals longer rain duration may be associated with the decreasing peak flow. Peat pipes are common in upland peat, it is possible that the peat pipes bleed the event water away. The longer rainfall event, the more likely peat pipes would have more impact on the flow. Also, the bigger scale the drain is, the bigger impact of these peat pipes would be.

Scatterplots of PC1 vs PC2 were plotted with blocking status and site on experimental catchment (Figure 3.16). There is very clear separation between zero order drains on the plots, i.e. the yellow and purple groups that represent events from drain CR6 before and after blocking. Two separate trend lines can also be seen for the CR5. These separate trend lines show the impact of the blocking on zero order drains. After blocking, the zero order drains were shifted towards higher peak flows.

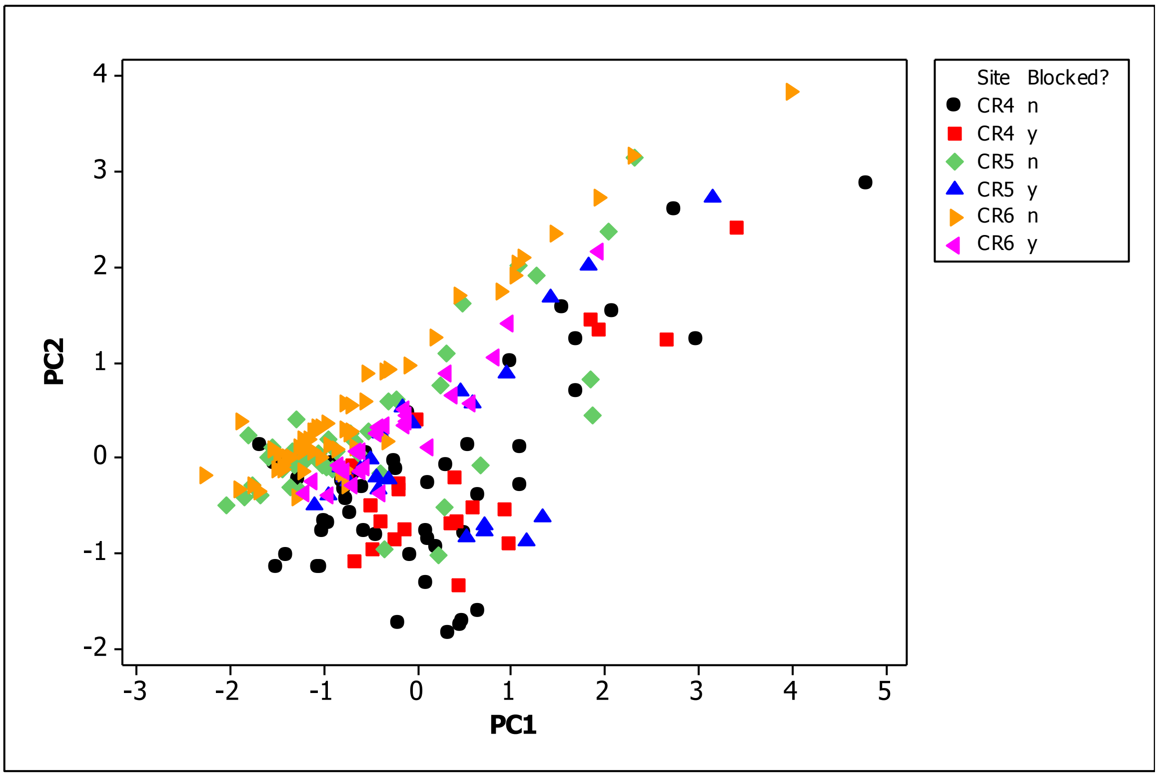

Figure 3.16: Score plot PC1 vs PC2 on experimental catchment.

However, this separation due to blocking can't be seen for the first order drain (Figure 3.16). Instead, overlapped plots for the first order drain and lack of separation of events before and after blocking indicate that drain blocking didn't necessarily change the event flow character on the first order drain. A lack of change in event flow character for the first order drain may indicate that there are more chances the peat pipes are operating at this scale. The existence of peat pipes would lead to the event water going through the subsoil pathways and so be unaffected by blocking.

The separation of the different scales observed on PC2 can also been observed by the score plot of PC3 vs PC2 and score plot of PC4 vs PC2 (Figure 3.17 and Figure 3.18). However, the same separation cannot be observed for either PC3 vs PC1 or PC4 vs PC1. Following the earlier analysis of principal components (Table 3.5), PC3 represents for increasing flow lag time and decreasing rain intensity, and PC4 represents the DOC concentration changes.

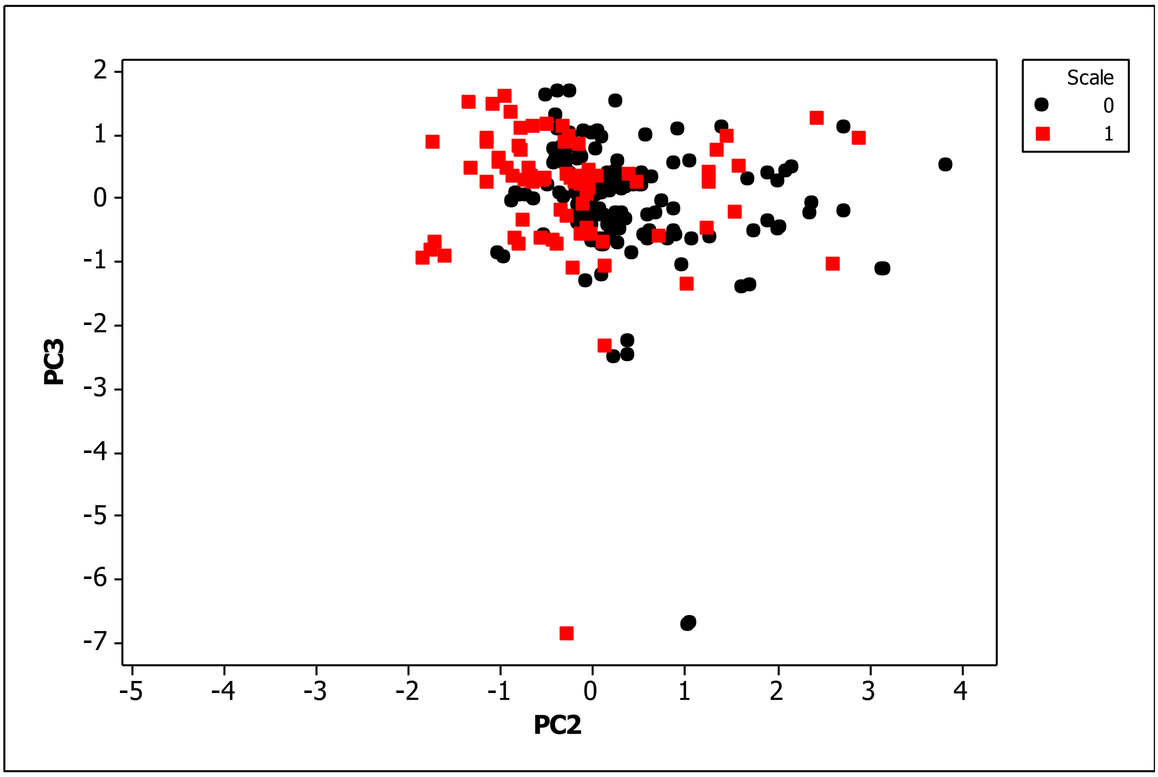

Figure 3.17: Score plot PC3 vs PC2 on experimental catchment.

On Figure 3.17, the majority of the events plot on the positive end of PC3 while a separation between first and zero order was made on PC2. Among all the events that were selected in this analysis, the contributions of the flow lag time to the events concentration changes increases with decrease of rainfall intensity. Relationship between rainfall intensity and flow lag time may indicate the general effects of the blocking, especially flow lag time seems increased after blocking. It should be noted that both Figure 3.17 and Figure 3.18 were selected to represent the scale differences and the differences due to blocking status are not highlighted.

Given the interpretation made above for individual components (Table 3.5), PC2 identified events are where peat pipes contributed on the peak flow changes. The separation on Figures 3.17 and 3.18 then show that the first order drains mainly plot at the positive end of PC2. Patterns of zero order drains and first order drains in Figure 3.17 and 3.18 simply reflect the scale differences towards the peak flow events when peat pipes exist, i.e. the bigger scale the drain, the bigger influence of the peat pipe would become enhanced upon peak flow events.

From Figures 3.16 to Figure 3.18 the plots suggest that the peat pipes may have more importance in controlling the peak flow in the experimental catchments than blocking. The

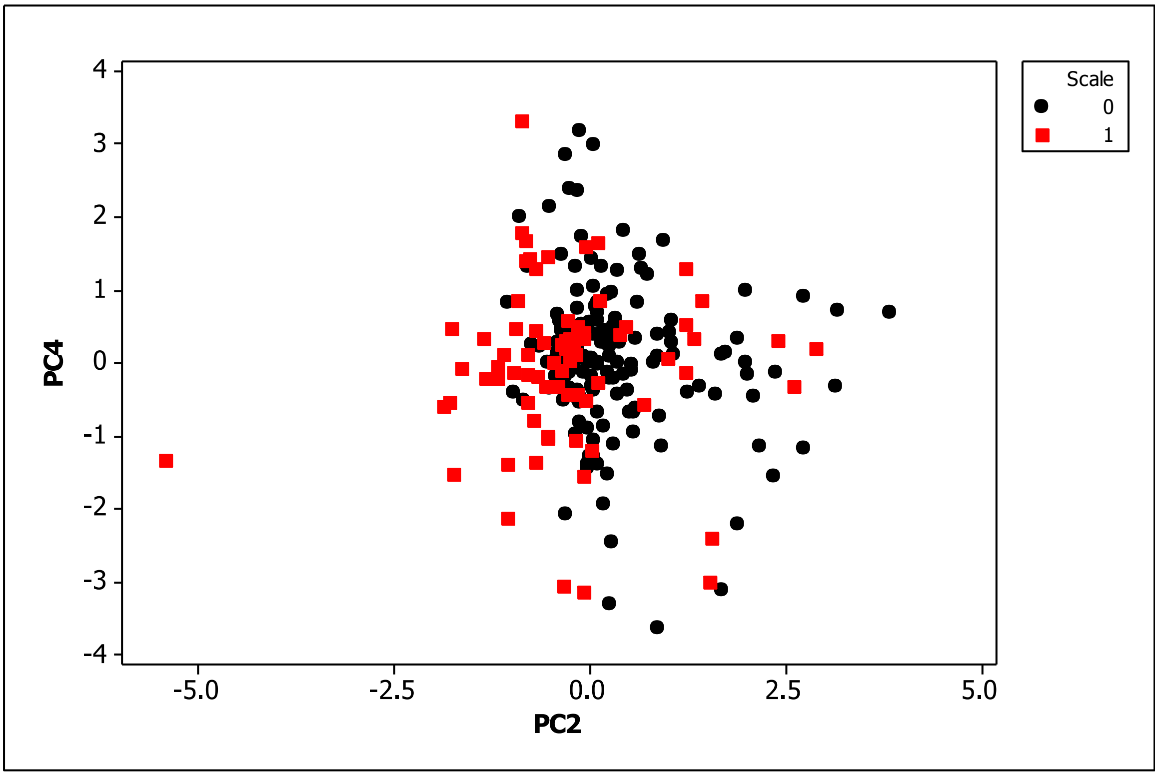

Figure 3.18: Score plot PC4 vs PC2 on experimental catchment.

different scale drains, the higher order drains were more likely to see the accumulated peak flow but at the same time are also more affected by potential existence of peat pipes. Therefore, drain blocking is more likely to fail to control the peak flow on the higher order drains in the control catchment.

In the experimental catchment, the blocking effects can be observed on the changes of flow lag time. Figures 3.19 and 3.20 show the comparison of the blocked and unblocked drains in terms of hydrological changes and flow lag time with rainfall intensity. PC1 represents the events when the peak flow increased with increasing rainfall while PC2 represents the events where peak flow decreased with increasing rainfall. In both situations, flow lag time increased with decreasing rainfall intensity after blocking while the unblocked periods have data plotting across the range of PC3.

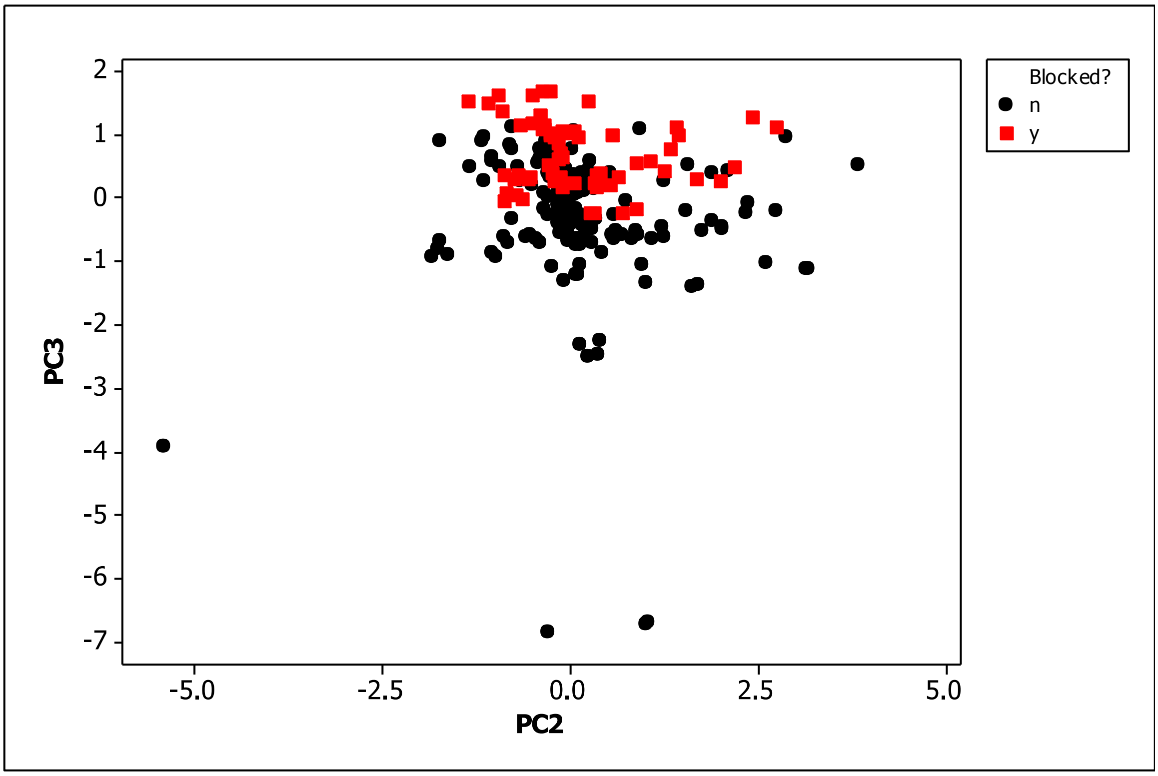

Figure 3.19: Score plot PC3 vs PC2 on experimental catchment.

The separation of blocked and unblocked event periods was less apparent when PC1 and PC2 were plotted against PC4. The small apparent separation on PC4 indicates blocking is less effective at altering the DOC concentration change across an event (Figures 3.21 and 3.22). Blocking is largely affected by the potential peat pipes which means it failed to maintain control on the peak flow in the higher order drain of the experimental catchment. Therefore, the variations of DOC concentration changes are less clear in Figures 3.21 and 3.22.

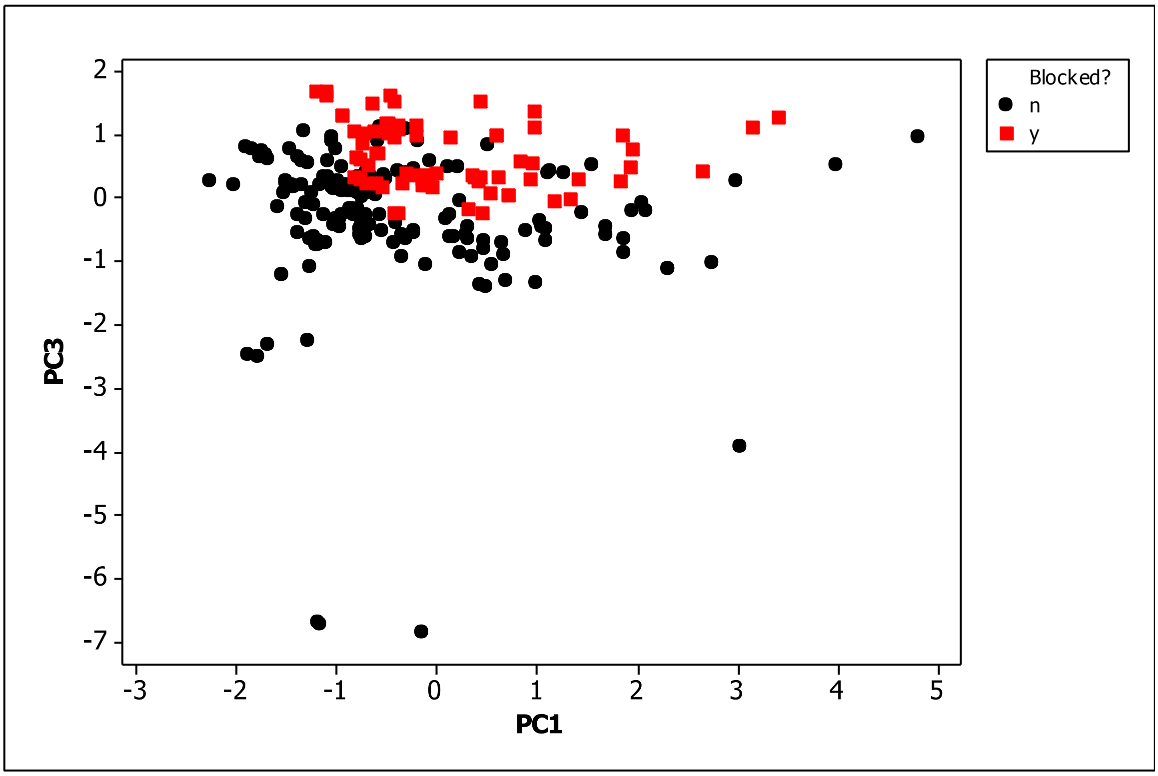

Figure 3.20: Score plot PC3 vs PC1 on experimental catchment.

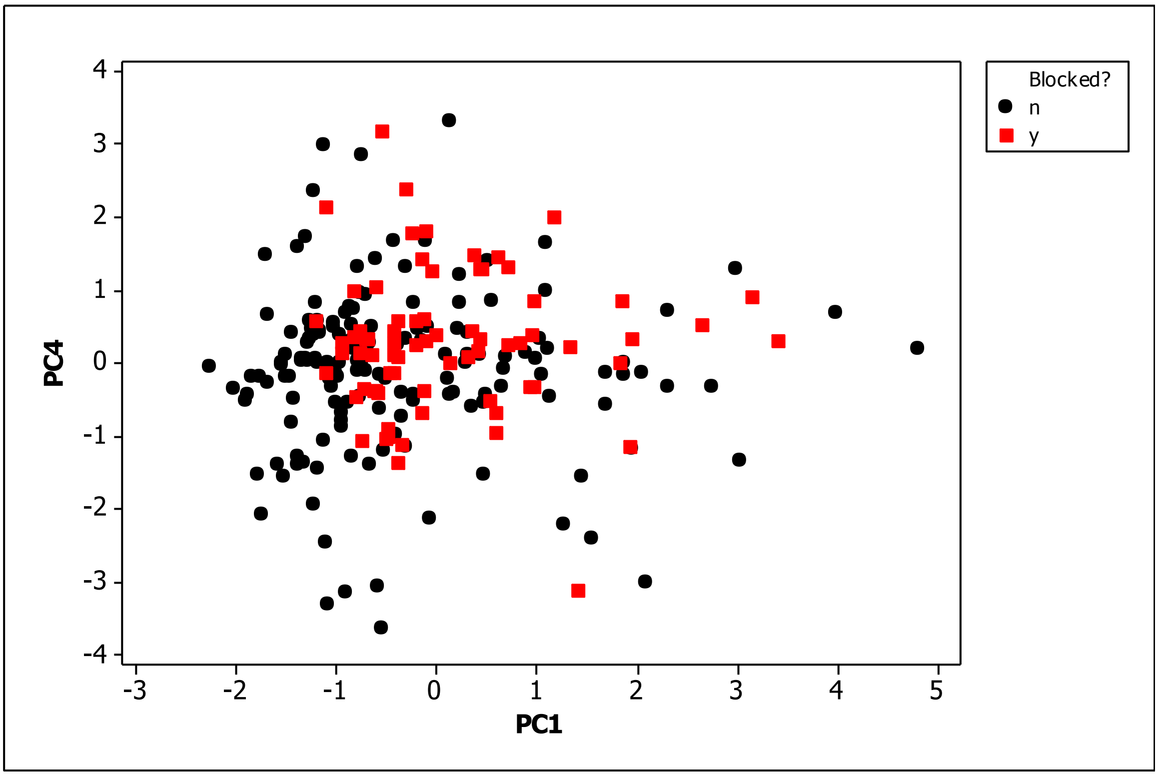

Figure 3.21: Score plot PC4 vs PC1 on experimental catchment.

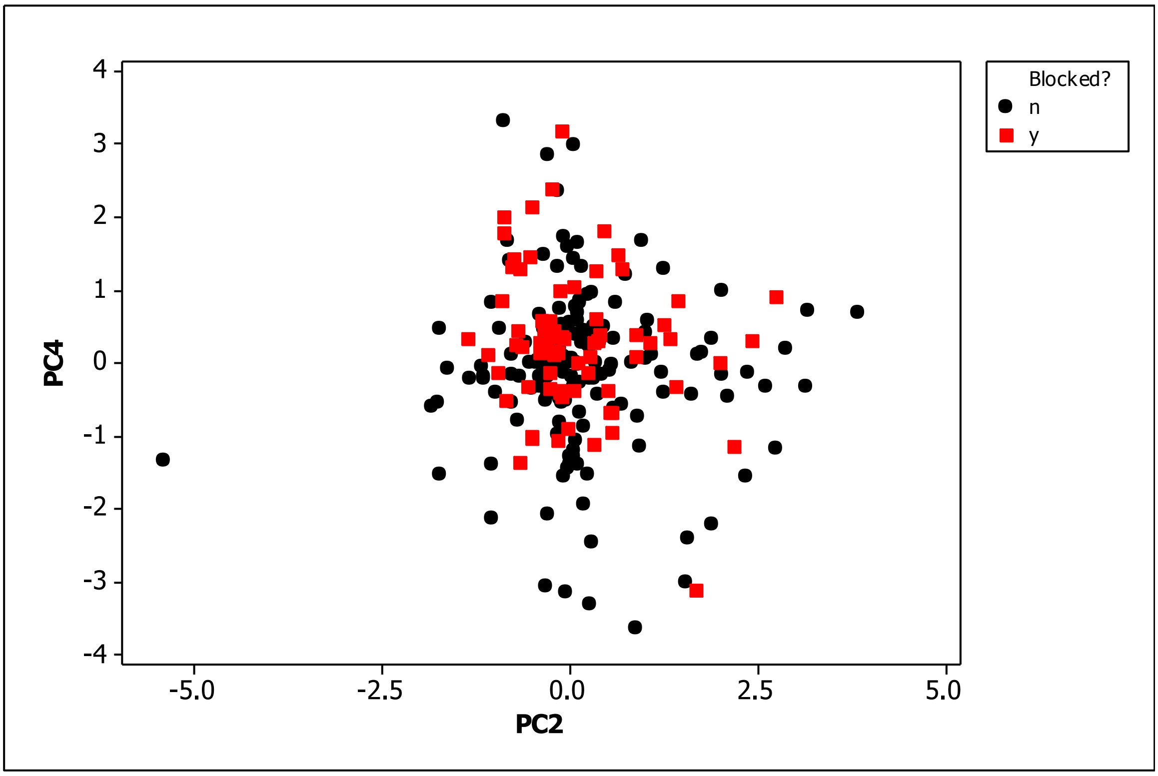

Figure 3.22: Score plot PC4 vs PC2 on experimental catchment.

3.5.3 PCA including other chemical parameters

To assess the potential flow path change that brings about the observed event flow and DOC concentration changes, a single PCA was performed including: pH, conductivity, DOC concentration, and applying the same rules described above (section 3.3). Upon analysis two principal components were selected. Together the two selected PCs explained 80.4% of the variance in the data (Table 3.9). The first component (PC1) is a contrast between pH and DOC concentration changes. The second principal component (PC2) has high negative loading for the conductivity. For PC2, the loadings DOC concentration change and pH are relatively small compared to that for conductivity; therefore, PC2 is dominated by the conductivity loadings.

Variable	PC1	PC2
DOC concentration	0.647	0.325
pH	-0.665	-0.202
Conductivity	0.373	-0.924
Eigenvalue	1.489	0.924
Proportion	0.497	0.308
Cumulative	0.497	0.804

Table 3.10: The first two principal components of Cronkley Fell.

Comparing PC1 and PC2 (Figures 3.23 and 3.24) confirms the interpretation of the components given above. The majority of the variation is parallel to PC1, i.e. variation only in DOC concentration changes. Separation gradually happens when moving towards the higher end of PC1, which indicated the inverse relation between two scales of the catchment and DOC concentration changes (Figure 3.23). Increases in pH occurred with increased scale. After blocking, the majority of the data plots at the negative end of PC2 which indicates an increase in event water conductivity after blocking (Figure 3.24).

Whisker-plots of pH and conductivity for both scale before and after blocking shows that in the zero order drains, both pH and conductivity increased after blocking. In the first order drains, pH of event water decreased while the conductivity increased after blocking (Figure 3.25 and Figure 3.26).

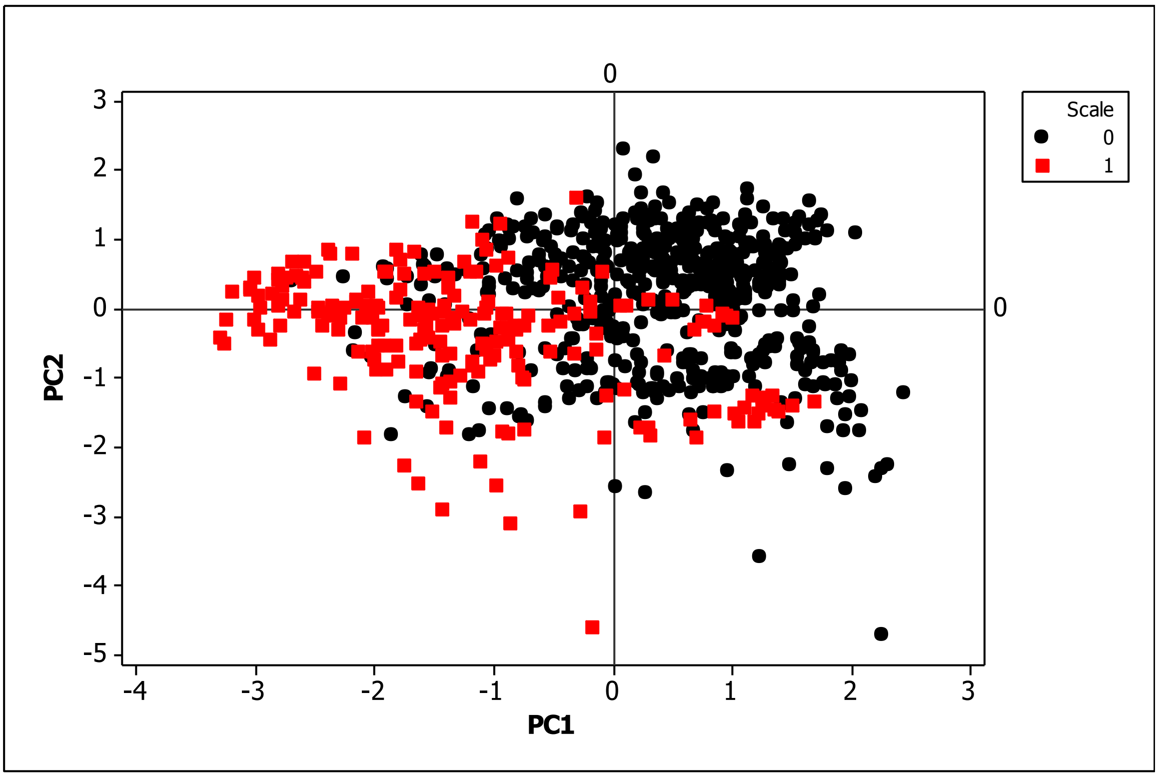

Figure 3.23: Score plots of PC1 VS PC2 on different drain scales.

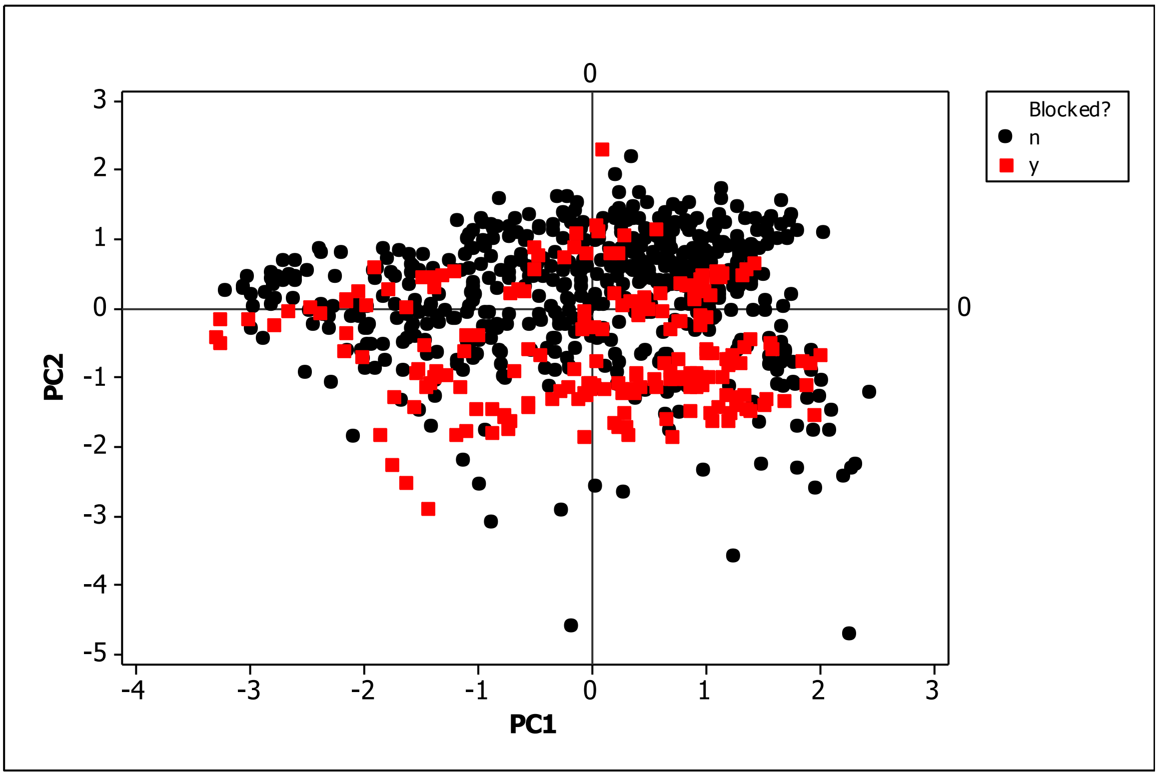

Figure 3.24: Score plots of PC1 VS PC2 on blocking statue.

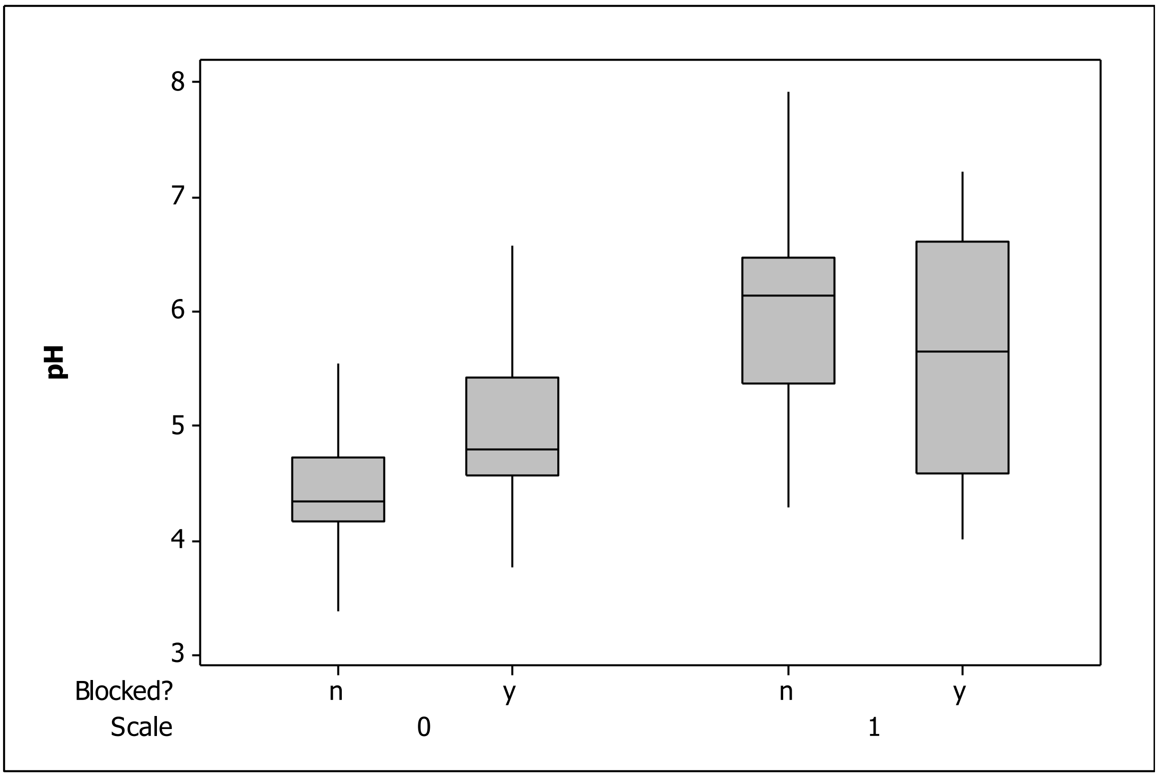

Figure 3.25: Whisker box of pH on two different scale drains before and after blocking.

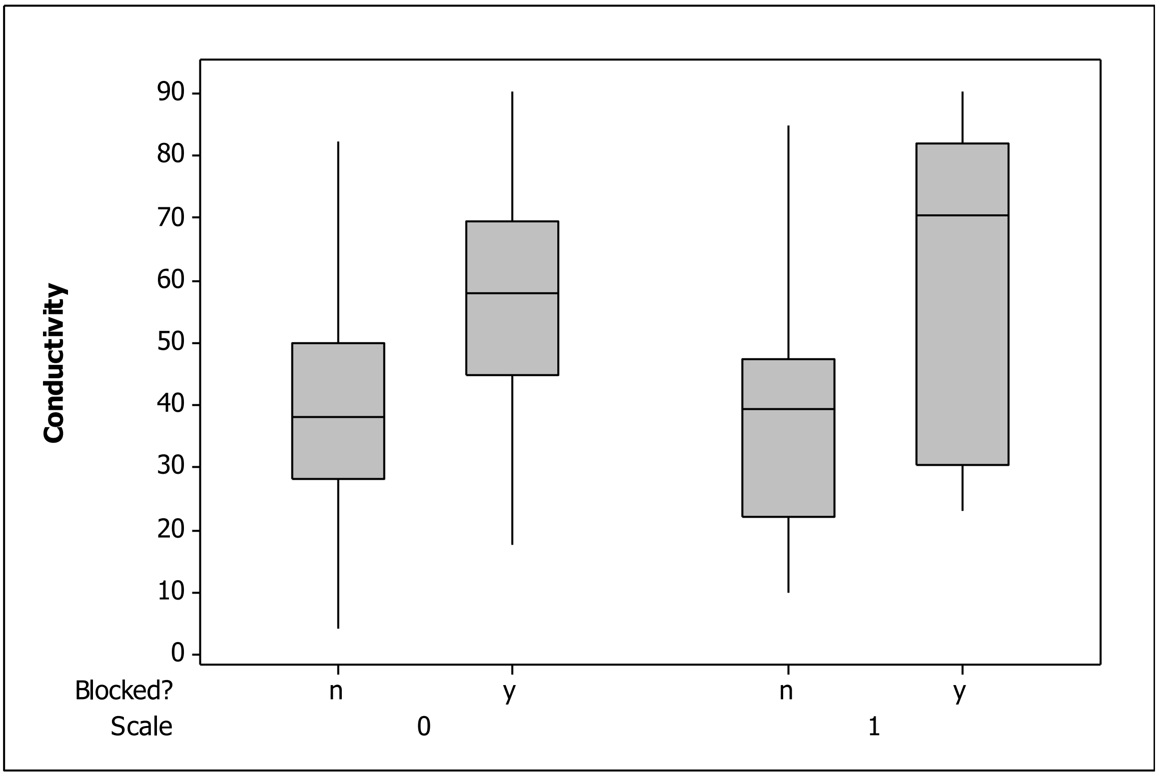

Figure 3.26: Whisker box of conductivity on two different scale drains before and after blocking

An ANOVA was applied on both PC1 and PC2 to investigate impacts of the experimental factors (Table 3.11). The majority of the variances of PC1 were explained by scale (38.7%). While PC2 mostly varies with blocking. This indicates the DOC concentration changes may be mainly controlled by the scale difference, while the blocking effects changed the conductivity. Worrall et al. (2002) found higher conductivity water was associated with 'old water', whereas the low conductivity at high flow represented the rain water. The shift from the new to old water after blocking among this events analysis may imply that the DOC composition changes, blocking brings event water that includes a greater component of deeper soil water.

PC1				PC2			
source	DF	P	Portion	source	DF	P	Portion
Month	1	<0.001	3.00%	Month		<0.001	1.61%
Scale	1	<0.001	38.74%	Scale		<0.001	5.15%
Blocked?	1	0.001	0.04%	Blocked?		<0.001	11.45%
Scale* Blocked?	1	<0.001	3.74%	Year		<0.001	2.02%
Error	751			Error			
Total	755			Total			
R-Sq =45.73%				R-Sq =20.79%			

Table 3.11: ANOVA of first two components.

3.6. Results of DOC flux

Variations of DOC flux changes over selected events can be observed on the whisker plot (Figure 3.27) before and after blocking. DOC flux changes over events decreased by 55.6% after blocking on both control and experimental catchments. During the peak flow events, rapid rain flow brought more rain water going through the system and, the DOC concentration decreased after blocking (Figure 3.4). As mentioned before, the events water went into the deep soil path ways in the higher order drains in the experimental catchment, which leads to the decrease in the peak flow. At the same time, the DOC concentrations changes were varied on a much bigger scale i.e. 400% variations during events. Therefore, although there are situations that both DOC concentration changes and event flow are decreasing, DOC flux changes can still been observed an average suppression of 55.6%.

Similar to the DOC concentration changes in the control catchment, the DOC flux changes also show differences between different scales in the control catchment (Figure

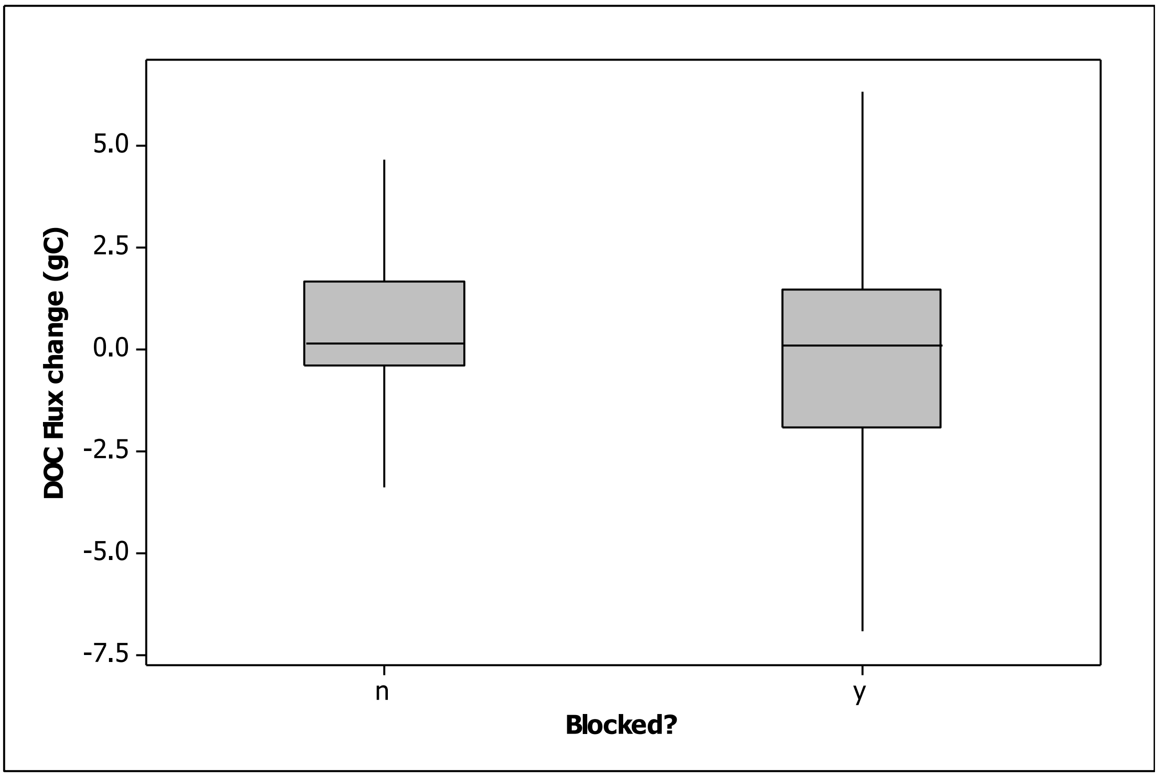

Figure 3.27: DOC flux changes before and after blocking.

3.28). Only this time, the flux changes seem much bigger in zero order drains than the first order drain. The differences in flux changes could simply be following the same depression of DOC concentration changes observed in the control catchments (Figure 3.4). The decline of flux changes from zero order drain to first order drain could be caused by two potential event flow changes: either the event flow would be increased from zero order drain to first order drain, or the decline of the event flow should be much smaller compared to the decline of concentration changes from zero order to first order drain. The smaller changes in event flow in the control catchment in turn indicate that the DOC concentration changes

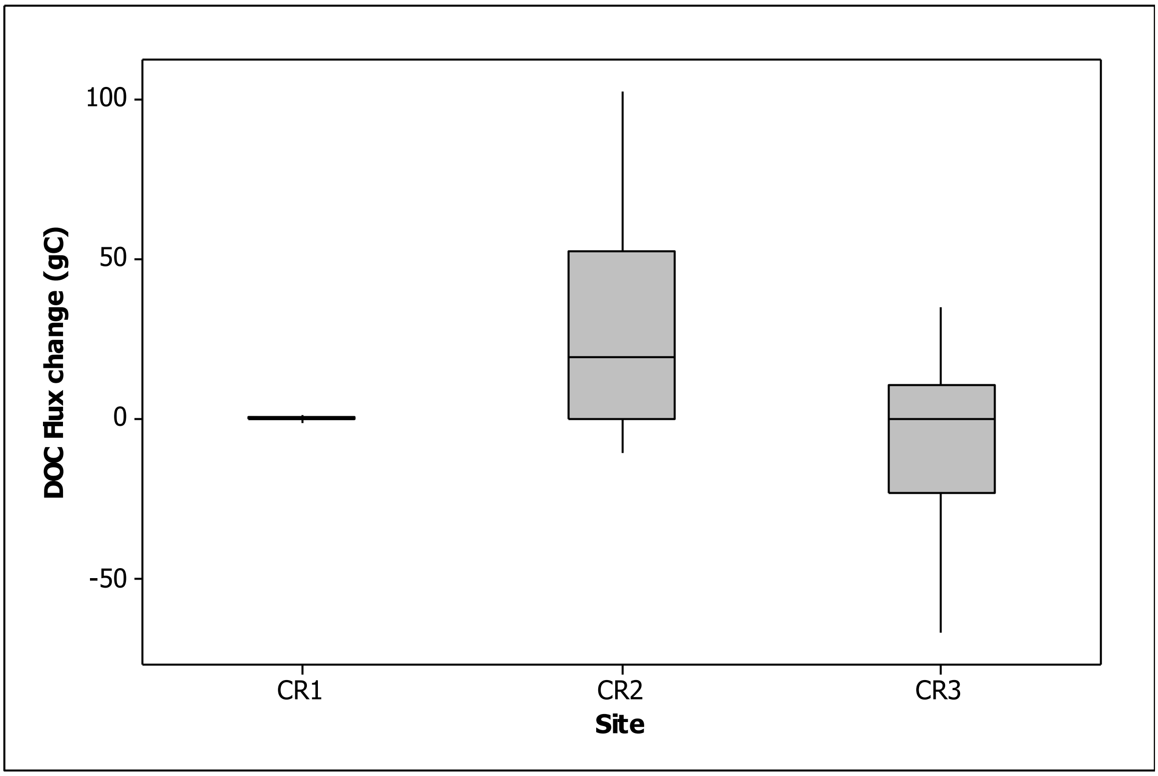

Figure 3.28: DOC flux changes in control catchment. The upper whiskers (top 25% of data) of CR 1 is too close to up boundary of interquartile box to shown in figure, which duo to the lower data point compare to other two drains.

are caused by scale difference between two different scale drains. A further PCA was then performed on the data set.

The comparison of the DOC flux changes before and after blocking in experimental catchment in between two scales is showed in Figure 3.29. In Figure 3.29, CR4, a first-order drain, the DOC flux change over events is smaller after blocking. Although CR5 and CR6 are zero order drains, only CR6 shows the same change as the first order drain. Instead of showing smaller changes as its paired drain, CR5 showed bigger, positive flux changes after blocking. By comparing to the DOC concentration changes in Figure 3.7, it is clear that DOC concentration changes were getting smaller in all three drains in experimental catchment. The increased DOC flux in CR5 indicated more of a difference that caused by the drain itself, as mentioned above, i.e. the presence of peat pipes. The existence of peat pipes would cause event water to run through sub soils. These flow path changes would minimize the impact of blocking. Both CR4 and CR6 show a minor decrease of changes of fluxes across the events duo to blocking and this must reflect flow path changes. In some extreme cases, like CR5, blocking will lost its feature as efficiently provide a more stable water flow during the events. Instead, it is more likely the events flow in CR5 would run through subsoil through the peat pipe which eventually caused the decrease of event flow. Both the DOC concentration changes and events flow decreased during the events, the rapid decline of

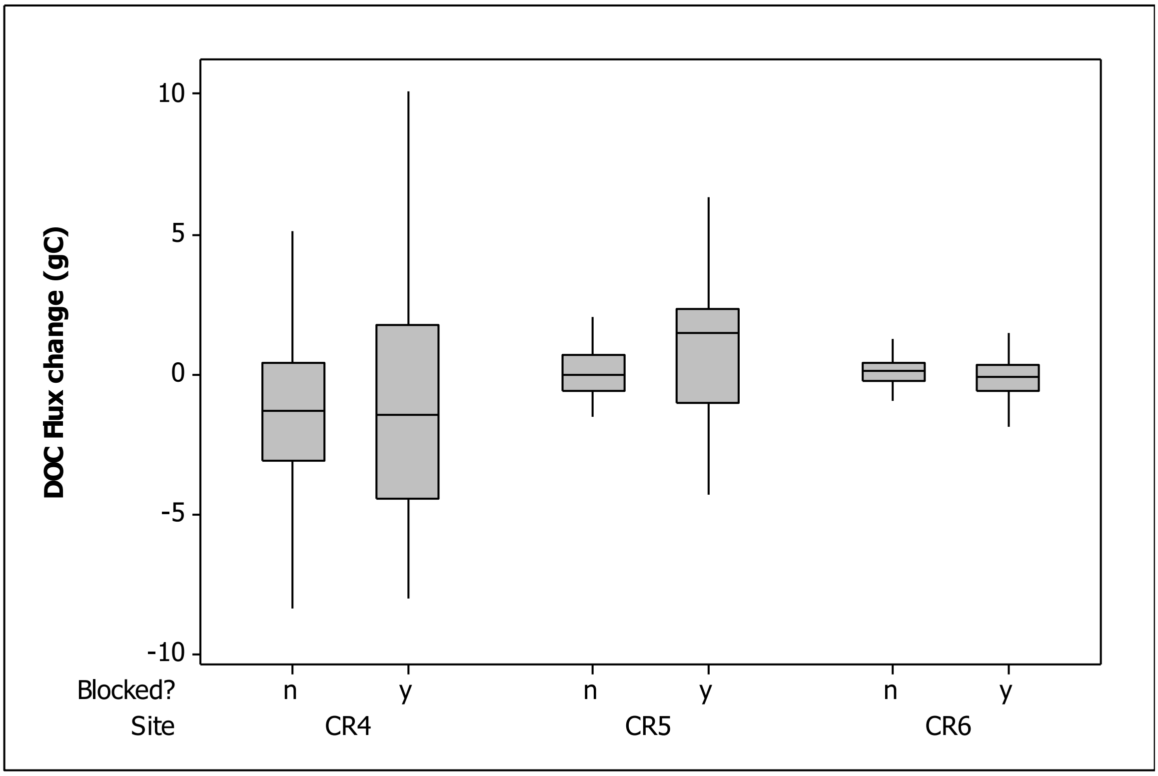

Figure 3.29: DOC flux changes in experimental catchment.

event flow lead to the increase of the flux changes.

Figure 3.30 shows the relative DOC flux changes on zero and first order drains during the unblocked and blocked periods. The comparison of the two Figures shows a contrasting result of relative DOC flux changes on different order drains. There was 78.6% decrease in DOC flux changes after blocking for the zero-order drains. Over the same period, the DOC flux from the first order drains increased by 42.2% after blocking. Over all, the relative DOC flux changes decreased 99.8% after blocking in both order drains (Figure 3.31). The huge difference in the relative DOC flux changes between zero order drain and first order drains may indicate large flow path changes. The event water seems to be going through the subsoil in the first order drains during the peak flow conditions. Similar to relative concentration changes, the catchment size played a more important role than the blocking itself. As earlier analysis revealed, there may be a considerable site difference between control and experimental catchment. Therefore, the control and experimental catchments' site difference may not be as comparable as some other studies revealed (Turner et al.,

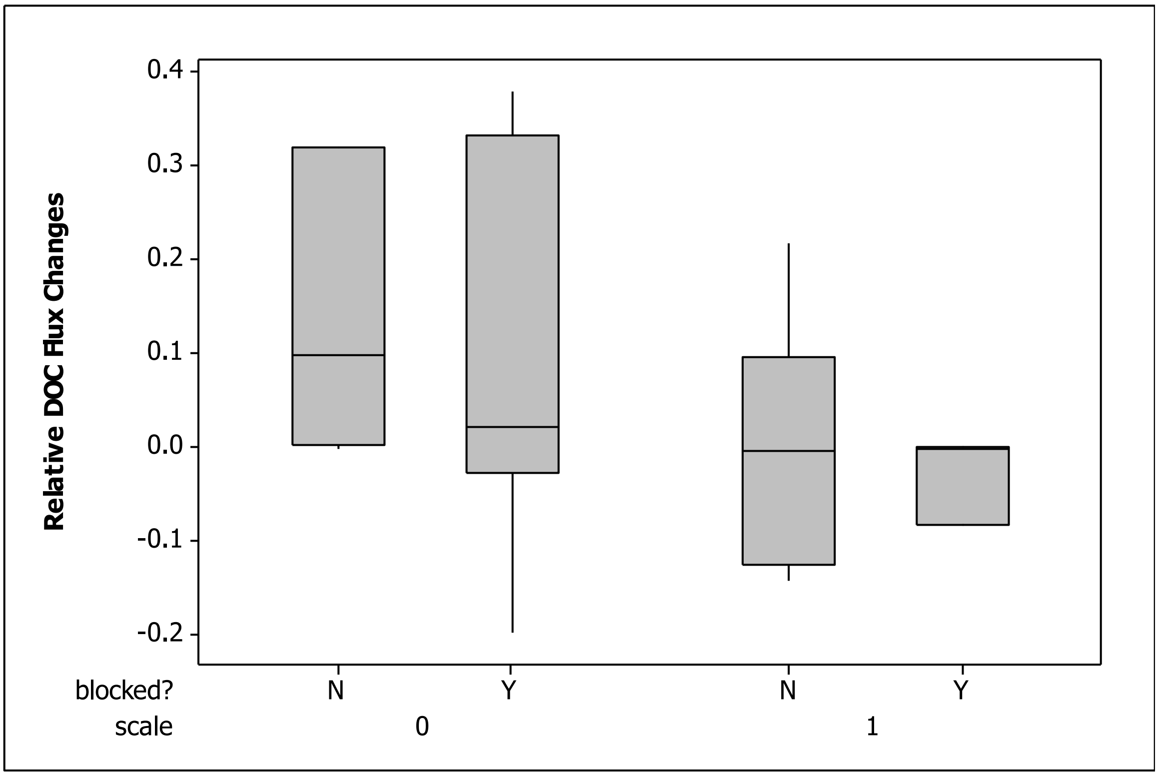

Figure 3.30: Relative DOC flux changes before and after blocking in both scales. The upper whiskers (top 25% of data) of unblocked drains in both scales are too close to up boundary of interquartile box to shown in figure.

2013). The relative data between control and experimental catchment may not accurate cover the changing trend of DOC flux changes before and after blocking.

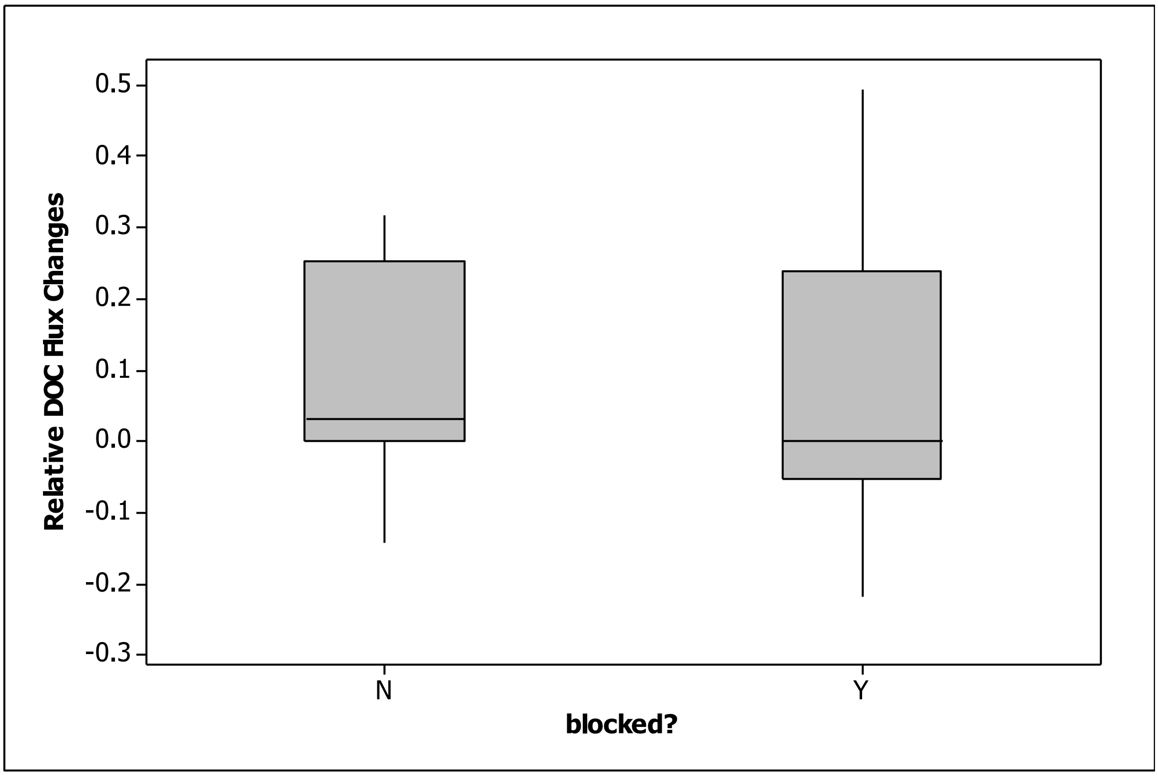

Figure 3.31: Relative DOC flux changes before and after blocking.

3.7. PCA of the hydrological changes during events

The first four principal components had eigenvalues greater than one, and the first principal component with an eigenvalue less than one was also selected. The first four components together explained 76.8% of the original variance in the dataset, while PC1 and PC2 explained about half of the original variance. All the data was z transferred and therefore PC1 represents a major interaction between rainfall total, rainfall duration and peak flow, antecedent flow rather than variable normalization. PC2 is controlled by positive loadings of peak flow, antecedent flow and negative loadings of rainfall total and rainfall intensity. PC3 is determined by a pair of strong positive loadings: flow lag time, DOC flux changes. PC4 is represented by high positive loadings of rain intensity and DOC flux changes. A similar hydrological behavior was performed here to the early analysis of the DOC concentration changes (Table 3.5). According to the dominant loadings of four components, PC1 represent the positive effects of direct rain fall to the event flow. PC2 demonstrates a negative relation between rainfall and events flow, events flow is more controlled by its antecedent flow and additional contribution from other sources rather than rainfall. As for the PCA of DOC concentration changes, the PC1 and PC2 group together and represent the hydrological changes while the PC3 and PC4 group together and represent the DOC flux changes.

Variable	PC1	PC2	PC3	PC4
Z Rain Total (mm)_	0.521	-0.434	-0.1	0.009
Z Rain Duration (hours)_	0.527	-0.416	0.008	-0.161
Z Rain Intensity (mm/hour)_	-0.058	-0.059	-0.487	0.756
Z Flow lag time	0.222	0.145	0.599	0.112
Z Peak flow	0.389	0.535	-0.043	0.129
Z Antecedent flow	0.405	0.547	-0.1	-0.002
Z Time between events	-0.288	0.058	0.231	-0.139
Z DOC flux changes	0.017	-0.159	0.573	0.595
Eigenvalue	2.1077	1.7682	1.2939	0.972
Proportion	0.263	0.221	0.162	0.121
Cumulative	0.263	0.484	0.646	0.768

Table 3.12: Hydrological loadings of first four PCs.
Where absolute loading values bigger than 0.400 were considered as dominate loadings and marked red.

In Table 3.12, PC3 represents the positive relationship between flow lag time and DOC flux changes, the DOC flux change increase with increasing flow lag time which may indicate the effects of the blocking. Loadings of PC4 highlight the interaction between rain intensity and DOC flux changes, the intense rainfall contributes to the positive DOC flux changes.

In the first group PC1 vs PC2, the divisions between the rainfall and events flow on

PC2 suggest that PC2 may indicate other sources or caused the increase of the event flow. Similar relationship between loadings of event flow and rainfall is also observed in the PCA of DOC concentration changes (Table 3.6). Brown et al. (1999) stated the contribution of rapid shallow flow to the events water is more likely to cause the DOC changes of events water than the changes in rainfall causing changes in the DOC flux change. This is especially so when the events water was mostly alter by the high intensity rainfall with the influence of the rainfall is often inversely related to the catchment size. The observations of PC1 and PC2 in both DOC concentration changes and DOC flux changes were most likely reflected by the same mechanism as Brown et al. (1999) proposed. PC1 represents the contribution of high intensity rainfall to the event flow and therefore contributed to the DOC flux changes. Loading from PC2 therefore represented the rapid shallow flow changes which contributed mostly to the event flow.

When blocking is applied to the sites, the results for DOC concentration changes suggested a positive effect due to events flow. In term of DOC flux changes in this section, it is expected a similar impact of the blocking may also reflects on the loadings. To test this hypothesis, an ANOVA was performed on the all four PCs with the changes of hydrological variances. Comparisons of ANOVA results in the first two components are listed in Table 3.13. In PC1, only peak flow, antecedent flow, rainfall intensity and flow lag time were found to be significant factors which in total explained 76.74% variances of PC1. Among these four significant factors, rainfall intensity explained majority of the variances (74.35%), while flow lag time explained the smallest of variances only 3.25%. In PC2, rainfall total, peak flow, antecedent flow, scale, blocked, rainfall intensity, flow lag time together explained 98.98% of the variance. Among the significant factors in PC 2, rainfall total explained more than half of the total variance (51.90%). Scale explained only 0.13% of the variance of PC2 which is the least important factor in the PC2. Comparison between PC1 and PC2 indicates blocking effects is limited on PC1 while it is significant on PC2. It is clear ANOVA of PC1 reflected contribution of the high intensity rain fall to the events flow as both the rainfall intensity and peak flow are among the significant variances.

The difference between PC1 and PC2 is mainly on the variance of scale and blocking. Scale is not a significant factor of the variances of PC1 while it is a significant factor in PC2.

Component	PC1			PC2		
Source	DF	P	Portion	DF	P	Portion
Rain Total	NS	NS	NS	1	<0.001	5.19%
Peak flow	1	<0.001	4.19%	1	<0.001	15.43%
Antecedent flow	1	<0.001	7.27%	1	<0.001	21.67%
Scale	NS	NS	NS	1	<0.001	0.13%
Blocked?	NS	NS	NS	1	<0.001	0. 76%
Z Rain Intensity	66	<0.001	74.35%	66	<0.001	7.93%
Z Flow lag time	10	<0.001	3.25%	10		1.34%
Error	331		10.94%	328		0.85%
Total	409			409		
	R-Sq = 81.18%			R-Sq = 99.16%		

Table 3.13: ANOVA of first two principal components, NS: not significant variances.

Variances between PC1 and PC2 reflected the hypothesis of the identification of each component earlier, which PC1 reflects the events high intensity rainfall dominated the event flow and PC2 reflects the event of rapid shallow flow, which dominated the event flow. Differences of two kinds of flow events are reflected by the blocking effects. In the events of high rainfall intensity dominated events, the blocking is not a significant factor contributing to events, nor is the scale factor. As an observation of Brown et al., (1999), scale should be an important factor during the high intensity rainfall. A one way ANOVA of PC1 with scale as a factor found scale is still a significant factor contributing to PC1 which explained approximately 10% of variances of PC1. It is only when the blocking has been introduced to the ANOVA that scale, blocking or interaction between these two were found not be significant. As the blocking is a significant factor contributing to the variance of PC2, it is therefore highlighted that positive blocking effects during the event flow are limited to the rapid shallow flow contribution. While similar effects (blocking) may be applied to high intensity rainfall events such as PC1, blocking effects may only eliminate the scale effects that may have brought on the event flow, but overall were not as an efficient control of the event flow itself. That means in PC1 blocking may have brought up the water table depth in both scales of drains which eliminated the potential scale effect on the events flow during the high intensity rainfall, but blocking would have failed to control the event flow as both scales of drains would quickly have overflown the potential buffer supplied by the drain blocking.

In PC3, antecedent flow, blocking, rainfall intensity, and flow lag time together explained 79.05% of the variances. Rainfall intensity in PC3 explained half of the total variance, while blocking explained the least of variances (6.89%). In PC4, peak flow, antecedent flow, scale, blocking, rainfall intensity and flow lag time together explained 93.50% of total variances. Rainfall intensity in the PC4 explained 83.11% of the variance. Scale is the least important factor among all the significant variances as it only explained 0.98% of the variances.

Component	PC3			PC4		
Source	DF	P	Portion	DF	P	Portion
Z Peak flow		NS		1	<0.001	0.0226
Z Antecedent flow	1	<0.001	0.0976	1	<0.001	0.0266
Scale		NS		1	<0.001	0.0098
Blocked?	1	<0.001	0.0689	1	<0.001	0.0526
Z Rain Intensity	66	<0.001	0.5251	66	<0.001	0.8311
Z Flow lag time	10	<0.001	0.2119		<0.001	NS
Error	331		0.2308	339		0.0574
Total	409			409		
	R-Sq = 83.05%			R-Sq = 97.20%		

Table 3.14: ANOVA of principal component 3 and 4, NS: not significant variances.

PC3 and PC4 indicated that rainfall intensity is the key factor that controls the DOC flux changes (Table 3.14). Blocking is expected to be an efficient land management appears to control the event flux. As shown in the Table 3.13, the blocking effects are significant but the majority of the flux changes are still controlled by the rainfall intensity. In other words, the blocking may not be as efficient as expected for controlling the DOC flux changes when compared to the characteristics of the event itself. The above section of DOC concentration changes (section 3.2) took the hypothesis that an additional flow path may be involved in the land management, which leads the event flow drain through the additional flow path (i.e. peat pipes). This hypothesis maybe also applied to analysis of the DOC flux changes here, the effects of the blocking is limited by the potential flow paths.

3.7.1. Comparison of PCs in control catchment

The score plots of PC1 against PC2 identified four end-members – a, b, c, and d (Figure 3.32). The direction of ab generally represents the zero order drains (CR1, CR2), while the cd trend is gathered by the zero order drains (CR3). The comparison of zero order drains and first order drains found loading plots of first order drains exist both in area ab and area cd. On Figure 30, end-member a has the lowest score on PC1. As mentioned earlier, PC1 is dominated by strong positive loadings of total rainfall, rainfall duration, peak flow and antecedent flow. End-member b has the lowest score on PC2, which is marked by high event flow, low rainfall events. End-member c has highest score on the PC2 and end-member d has the highest score on PC1. The details of the four individual end-members are given in Table 3.15. It is found in Table 3.14, that all four end-members a, b, c, d are exactly same as the earlier analysis in DOC concentration changes in Table 3.6. The trend line of zero order drain (Line ab) and the trend line of first order drain (Line cd) were exactly the same as the study of the control catchment in the analysis of DOC concentration changes (Figure 3.9). The patterns of two Figures are rotated 90 degrees by the differences of two PC 2s, the earlier one has the positive loadings of rainfall total and rainfall duration and negative loadings of peak flow, antecedent flow (Table 3.5), but the current one has the positive loadings of peak flow and antecedent flow and negative loadings of rainfall total and rainfall duration (Table 3.11). The result of the earlier analysis can therefore imply the following here: during the hydrological peak flow events the event flow is determined by the different rainfall intensities and differences of the flow lag time. The flow lag time is determined by the different scale of the drains. The study also indicates that the potential flow path would also influence on the event flow typically on the higher order drains. In the Figure 3.32, the almost paralleled lines among higher order drain that moves between line ab and cd indicates this potential of the other flow paths causing the event flow to decrease.

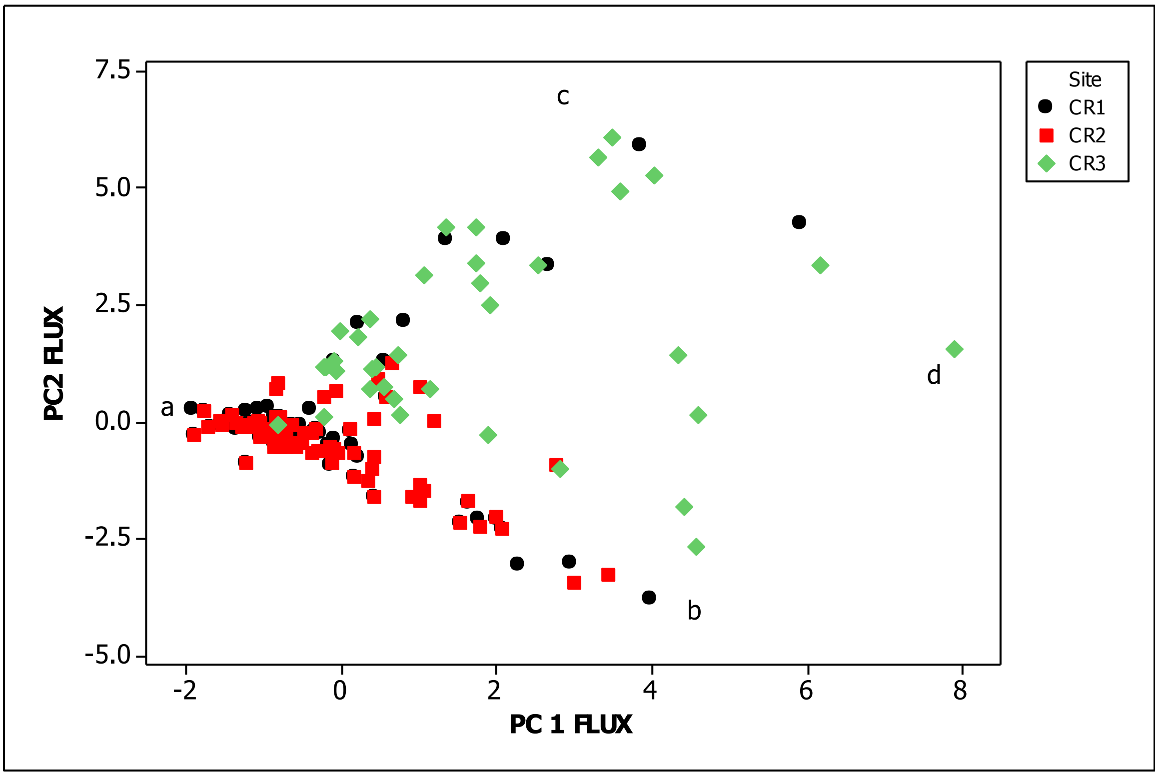

Figure 3.32: Plots of PC1 VS PC2 on control catchment.

End-member	Date	Site	Scale	RT	RD	RI	FLT	PF	AntF
a	28/03/2008	CR1	0	0.20	0.20	1.0	1.00	0.0005	0.0005
b	04/08/2008	CR1	0	28.8	28.8	1.0	1.25	0.0005	0.0004
c	10/11/2008	CR3	1	0.60	0.25	2.4	2.00	0.3945	0.2672
d	04/08/2008	CR3	1	28.8	28.8	1.0	2.00	0.3247	0.2499

Table 3.15: Hydrological characters of the four end-members In control catchment
RT: Rainfall total (mm); RD: Rain duration (hour); RI: Rain intensity (mm/hour); FLT: Flow lag time (hour); PF: Peak flow (m^3/s), AntF: Antecedent flow (m^3/s).

Comparison of PC3 VS PC4 would show the DOC flux changes in the control catchment during the events, as both of two components including the high loadings of DOC flux changes. Despite six individual events in the first order drains, the majority of data plots in both order drains are moving towards the positive ends of both axes. As both PC3 and PC4 have the positive loading of DOC flux changes, DOC flux changes were increasing with increasing rainfall intensity and flow lag time in control catchment.

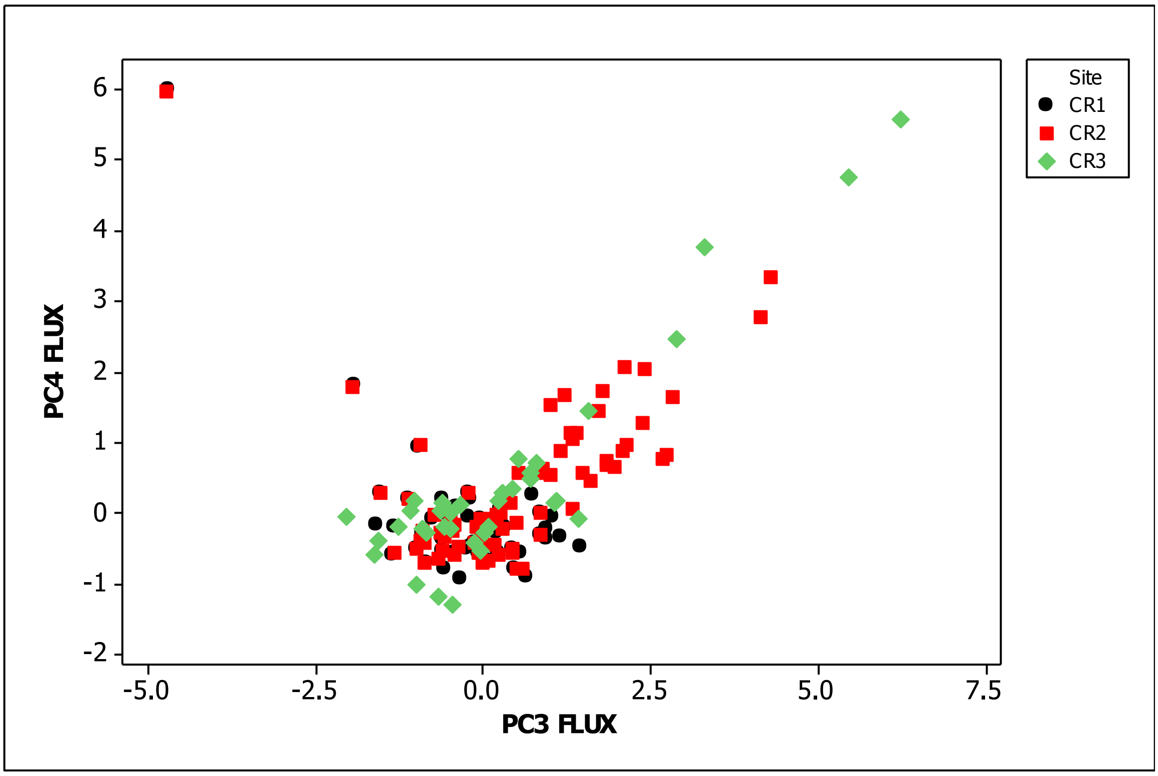

Figure 3.33: PC3 vs PC4 in control catchment.

3.7.2. Comparison of PCs in experimental catchment

Similar to the analysis of the data from the control catchments, the analysis of the data from the experimental catchment is based on the two separate groupings of principal components - PC1 vs PC2 dominated by hydrological characteristics and PC3 vs PC4 dominated by changes in DOC. In the plots of PC1 against PC2 (Figure 3.34), four end-members e, f, g, h were identified. As seen earlier, the four end-members are exactly as in Figure 3.15, therefore the values of individual end-member can be found in Table 3.9. Similar patterns between control (Figure 3.32) and experimental catchment (Figure 3.34) were observed before and after blocking. There are clear separations between blocked and unblocked periods in the zero order drains (CR5, CR6). Event flow changes before and after blocking in first order drain (CR4). As mentioned before, the unclear transition in first order drain implies there may be more influence of additional flow path on the first order drains,

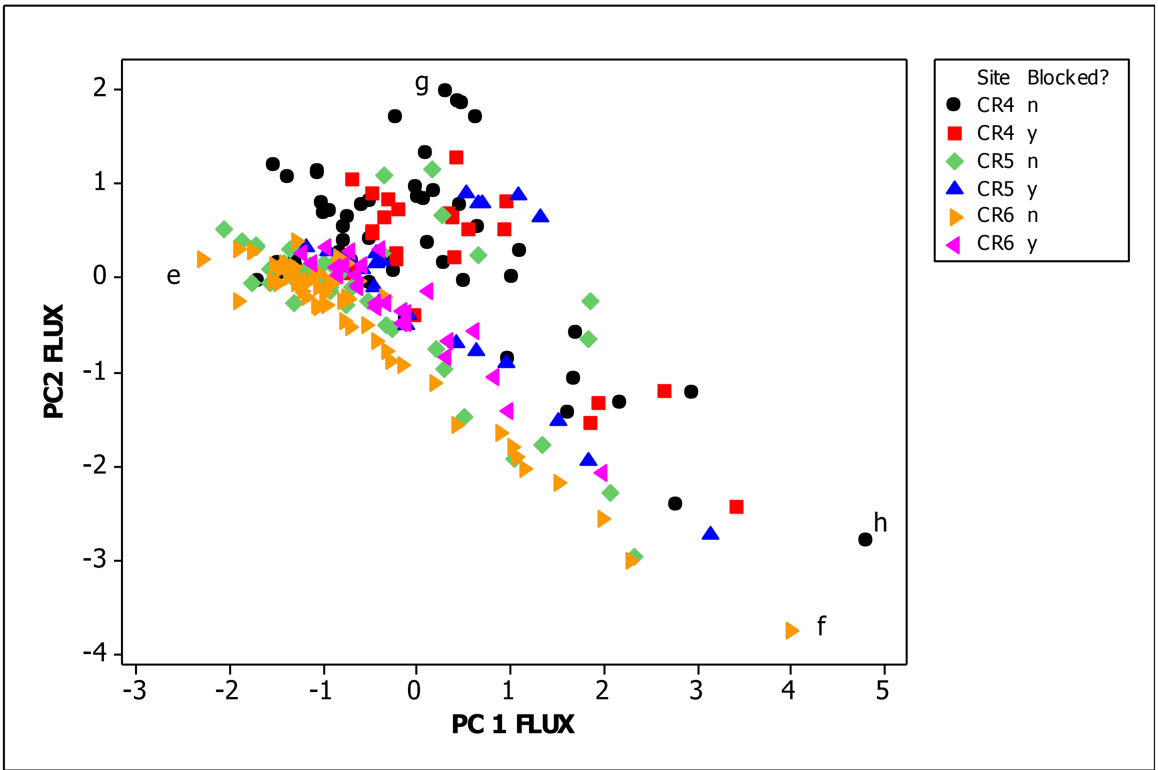

Figure 3.34: Plots of PC 1 vs PC2 before and after blocking in individual sites in experimental catchment.

which limited the blocking effects to maintain the stable water table.

Loading plots of PC3 against PC4 in experimental catchments (Figure 3.35) shows dramatic changes on patterns to that observed for the control catchment (Figure 3.33). With both order drains plotting at the end of the negative end of the PC4. The plots showing that both order drains were under the positive influence of rainfall intensity and flow lag time in the control catchment (Figure 3.33) are not obvious in the experimental catchment (Figure 3.35). Figure 3.35 shows the majority of the events were plotted at the negative end of PC4 and parallel to the axis of PC3. There are no clear separations between unblocked and blocked events at each site. Figure 3.35 suggested that the influence of the rainfall intensity on DOC flux changes were not present, i.e. there are no clear trends on PC4 axis. As shown on Figure 3.17, blocking have the positive effects on maintained peak flow changes in experimental catchment despite high rainfall intensity. In Figure 3.35, the DOC flux changes is also shown been less infected by rainfall intensity. In section 3.5.2, it has been shown that flow lag time increased after blocking. This is also shown in Figure 3.35 as the majority of data were parallel to PC3. However, there is no direct trend of DOC flux changes after blocking events through the blocking has shown a significant impact on changes in flow lag time. The potential flow path ways have appeared to limit the effects of blocking on DOC flux changes.

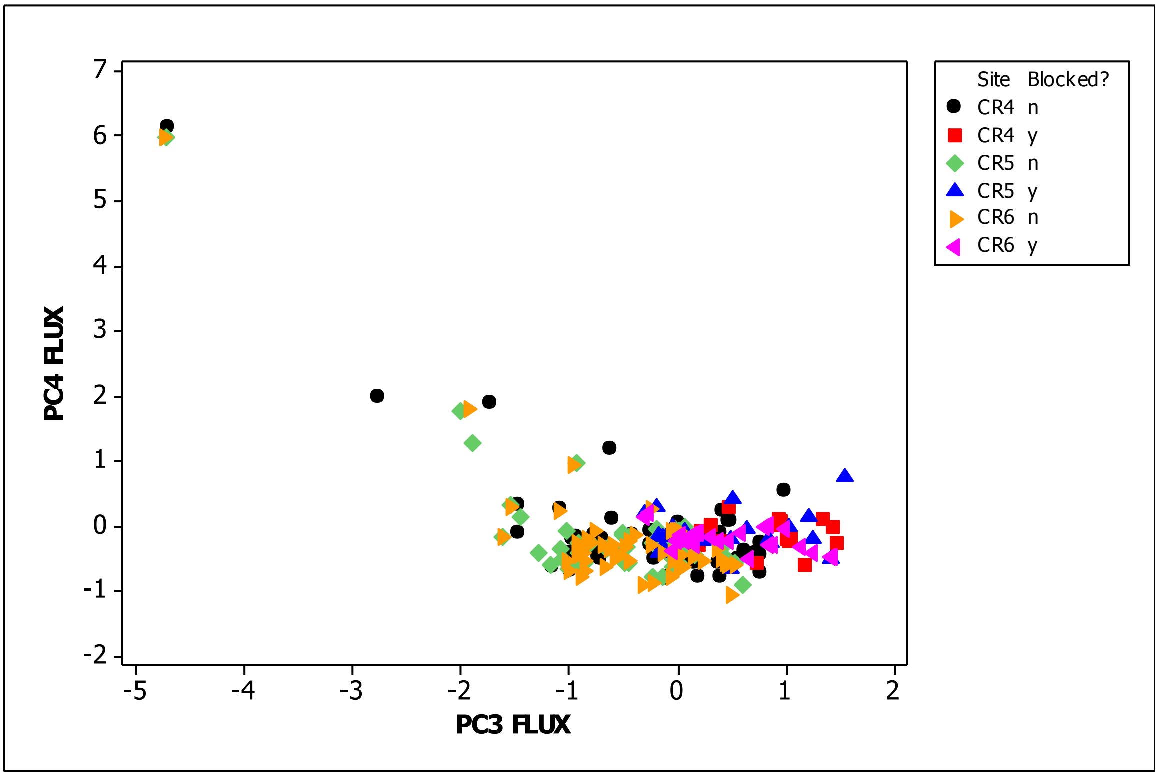

Figure 3.35: Plots of PC3 vs PC4 in experimental catchment before and after blocking in individual site.

3.7.3. Comparison of the pH and conductivity

To estimate the potential flow path changes, PCA were performed that included DOC flux, pH and conductivity. Two components were selected and together they explained

Variable	PC1	PC2
pH	0.639	0.418
Conductivity	-0.701	-0.028
DOC Flux	0.317	-0.908
Eigenvalue	1.1805	0.9941
Proportion	0.394	0.331
Cumulative	0.394	0.702

Table 3.16: First two components in terms of DOC flux.

72.5% of the data set (Table 3.16). PC1 represented the negative correlation between DOC flux change and pH. Loadings in PC1 are dominated by positive loading of pH and negative loading for conductivity. PC2 is made of the positive loading of pH and negative DOC flux changes. Therefore, PC1 stands for the event waters that have high pH and low conductivity while PC2 associated high pH event water to low DOC flux changes. This unusual observation compared to the general high conductivity associated with the high pH indicates that the mixture of event water, as it has been noticed that pH and conductivity trend to increase with peat soil depth (Holden et al., 2004). Event water is therefore a mixture of the rainfall, base flow water and deep soil water.

An ANOVA was performed on both PCs (Table 3.17). All the factors were found to be significant for both PC2. For PC1, all factor together explained 33.36% of total variance in PC1. Among all factors, scale explained the most variance (19.34%), while year only explained 0.26% of the variance. Month, blocked, and the interaction between scale and

	PC1			PC2		
source	DF	P	Portion	DF	P	Portion
Month	11	<0.001	4.76%	11	<0.001	1.94%
Year	2	<0.001	0.26%	2	<0.001	4.89%
Scale	1	<0.001	19.34%	1	0.003	3.57%
Blocked?	1	<0.001	6.08%	1	<0.001	13.95%
Scale* Blocked?	1	<0.001	2.88%	1	0.05	0.28%
Error	739			739		
Total	755			755		
	R-Sq =34.77%			R-Sq =26.25%		

Table 3.17: ANOVA of first two principal components.

blocked explained 4.76%, 6.08% and 2.88% of total variance respectively. In PC 2, the same factors were found to be significant and together they explained 24.66% of variances in PC2. Blocking explained the most of the variance in PC2 (13.95%) while interaction between scale and blocked was found to be the least important (0.28%). Month, year and scale explained 1.94%, 4.89% and 3.57% of the rest of variance, respectively. The difference of scale factor on PC1 and PC2 shows that the variances of scale may alter the observed mixture of different sourced event water. Blocking seems to lead to the high pH event water associated with low DOC flux changes. This shows that the blocking alters the flow paths which leads to the event water going through the deep soil which initially decreased the variation in the DOC flux changes.

3.8 Conclusions

Blocking was found to be a significant factor impacting both DOC concentration and DOC flux changes over runoff events. However, the effects of blocking during the peak flow events were more controlled by the flow path and scale within any catchment. Unlike the reverse relationship between the DOC concentration and scale shown by the Brown et al. (1999), this events analysis found the DOC concentration change over events increased with scale after blocking.

The results showed that the blocking was a significant influence on the DOC flux and DOC concentration changes over events by controlling the event flow. These event analyses found rainfall total and peak flow have the biggest impact on changing peak flow of the events. However, rainfall intensity and relationship between flow lag time and rainfall duration also alter peak flow throughout the events. When the rainfall duration is smaller than the flow lag time, the higher rainfall intensity the higher peak flow would be. When events have the same rainfall intensity, the higher order drain would have the higher peak flow. When rainfall duration is longer than flow lag time, the peak flow increased with scale.

The blocking method used here was based on peat dams, which, during the storm events, water would most likely overtop the dam and continuing running through the drain. Alternatives was to build a series of dams with the aim to encourage revegetation, therefore events water during significant flow events would overflow the drain cross the vegetation of the peat (Armstrong et al., 2012). Further studies would therefore concentrate on the vegetation restorations which may impacts on the DOC releasing.

Chapter 4 Revegetation

4.1 Introduction

The earlier chapters have discussed the role of peatland as a carbon sink and point out that peatland is a sensitive system that requires specific climate conditions and poor drainage to grow, develop and remain stable. Drainage in upland peat therefore would lead to a negative impact on the ecosystem and could lead to a transition from a carbon sink to a carbon source. Moreover, studies show that not only the drainage but also burning and grazing would not only lead to increases in surface runoff but also increased soil erosion, which would enhance the net dissolved organic carbon (DOC) export (Bellamy et al. 2012; Brown et al. 2015). Cutover surface plants (Evans and Brazier, 2005) or cool burning (Clay et al., 2009) have been shown to lead to either the absence of the vegetation or changes to the colonised vegetation. The absence of vegetation would lead to the exposure of the peat surface and elicit an increase in the number of runoff events to the stream especially during storms (Robroek et al., 2010). Moreover, land management, e.g. drainage, would enhance the runoff events as surface water flow is moving faster for the bare peat surface than for the vegetated surface. Thus the soil erosion will enhance on the bare peat which will also lead to increased carbon losses (Worrall et al., 2007; Strack et al., 2011; Peacock et al., 2013). The potential changes of vegetation following the extraction of the vegetation were also observed by several researchers (Palmer et al., 2001; Strack et al., 2011). Following the recolonisation of the vegetation, the changes of fractions of DOC may occur as the different fractions of DOC were linked to the different vegetation types, most noticeably in the changes to the coloured fraction of DOC (Peacock et al., 2013).

Alternatively, drain blocking could sustain a water table during drought periods and storm periods which initially would limit DOC export from the peat soil (Worrall et al. 2007). The stable water table could encourage vegetation and potentially lead to recolonization of areas of bare peat. Stable water table and changes to flow paths through and over the peat have resulted in decreased production of the humic DOC from deep peat (Wilson et al., 2011). Increased vegetation cover of the peat improves self-regulation of the acrotelm by retaining high moisture level beneath the plant canopies (Petrone et al., 2004), this can lead to the substantial stability in the high DOC export from the peat during the runoff events (Jager et al., 2009). Peacock et al. (2013) studied the natural revegetation after drain blocking and found that around the peat pools the revegetation has little influence on the DOC concentrations and it was on hill-slopes that DOC concentration change was greatest. Parry et al. (2012) demonstrated that surface roughness may play a more dominant role in terms of peak flow events. The transition from the bare peat to vegetated peat would yield greater storm flow changes in a river than blocked drains and thus the impact of blocking on the revegetation associated DOC concentration and export would also be limited.

Apart from impact of drainage on revegetation associated DOC concentration and export from peatland, other land management such as burning also lead to the changes of vegetation which would alter the thermal regime of the peat surface, leading to significant changes in carbon cycling and soil hydrology (Clay et al., 2009; Brown et al., 2015). Research based on drainage associated restoration (i.e. drain blocking) found there was no impact of revegetation upon DOC concentration and export change (Holden et al., 2007). The impact of revegetation after burning on the DOC changes were studied by Qassim et al., (2014) and found a significant increase in DOC concentration in the soil pore water of a revegetated site. However, as the study (Qassim et al., 2014) was based on the soil pore water, the impact of revegetation on the soil runoff water was still unclear. Although studies observed soil thermal regime varies with revegetation (Kettridge et al., 2012; Brown et al. 2015), and therefore leads to the changes in soil moisture, i.e. evapotranspiration changes, there are no observations drawn between the DOC change and the soil moisture or soil energy changes. Clay et al., (2009) indicated that managed burning does not correlate with the changes in DOC concentration, albeit the water colour was found to be related to the burning impact, again the potential following recolonization of vegetation and the potential DOC changes were not included. Therefore, the following chapter is focused a study on DOC concentration changes in runoff during revegetation after a managed burning on the study catchment.

4.2. Methodology

4.2.1 Study Site

The revegetation study was based at Killhope, Cowshill, County Durham, Northern England (Figure 4.1). An experimental and a control catchment were chosen with a meteorological tower and an automatic water sampler on each catchment. Both the experimental and control catchments have been burned where control catchment was left as bare peat and experimental catchment had been revegetated in August 2013. Both automatic water samplers were installed at the bottom of the stream gully in each catchment so as to sample catchment runoff. Details of the installation of auto samplers are as described in chapter 1.

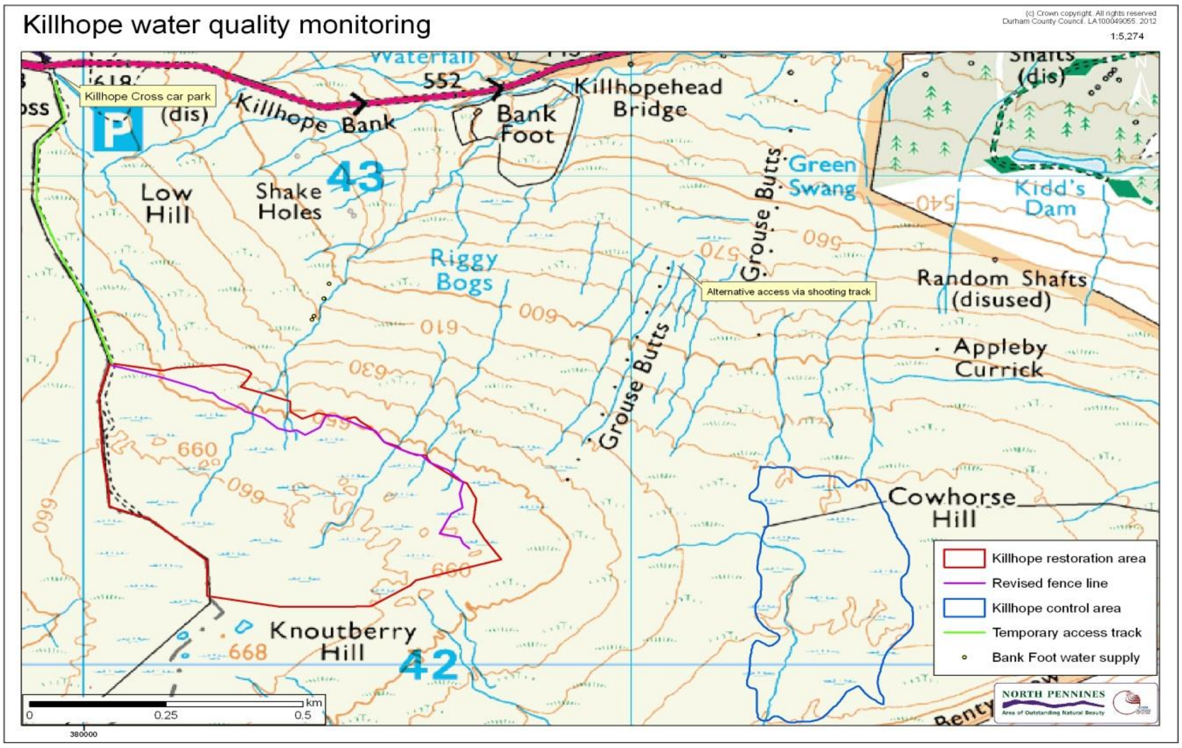

Figure 4.1: Location of study site, Killhope, Co. Durham (North Pennines, 2013).

The samplers were installed with a tube up to 3 m long so that the sampler could be located away from the stream channel to avoid flooding at peak flow. The tube was installed on the base of the stream in between two flat rocks to ensure the tube was taking the water sample from the stream base, while ensuring against being blocked by stream sediment. The samplers were preset to take water samples at least once every 24 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 48 hours due to site access restrictions. To mitigate against battery failure during the shooting and fledging seasons, an additional solar panel was installed on the top of the gully and linked to the sampler battery case through a 2 m long cable to provide sustained power charge to the sampler. 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. In both experimental and control catchments, the shallow stream flow (water table under 20 cm) were hugely influenced by the freezing and dry period, noticeably up to 45% of entire study periods were under the influence of the extreme weather and thus led to no sample being taken. On the other hand, the flow gauging that was used in chapter 1 and 2 to access the water flux was not suitable in this revegetation study because each gully floor had eroded through to the rockhead. Instead of using flow gauges, a meteorological tower was sited in both catchment to assess the changes in energy budget on both catchments.

Two meteorological towers were built on the top of each gully (experimental and control catchment). There was an average of 1.8 m vertical distance between the auto sampler and meteorological tower in both catchments. The two meteorological towers were from Campbell Scientific (Figure 4.2) and consisted of a 2 m tall tower above the surface with 1 m driven into the peat soil for stability. A net radiometer (NR-Lite, Campbell Sci, W/m^2) was installed on top of the poll. Two temperature (^oC) and relative humidity probes (HC2S3, Campbell Sci, %) were installed under the net radiometer. Distance between the two humidity probes was 1 m. A set of two self calibrating soil heat flux plate (HFP01-SC, Campbell Sci, W/m^2 mV) were installed 1 m apart from each other and 10 cm deep under the soil surface. A set of two pressure transducers for water depth measurement (PDCR1830, Campbell Sci, m) were installed in two dipwells to measure water table hourly. A tipping bucket rain-gauge (ARG100, Campbell Sci, mm) was also installed on the experimental site for the measurement of rain fall hourly. In the control catchment, the same settings of meteorological tower were applied, apart from a set of two temperature probe (T107, Campbell Sci, C) were used instead of heat flux to measure soil temperature hourly. Both the experimental and control catchments have been burned, where the control catchment was left as bare peat and the experimental catchment has been revegetated.

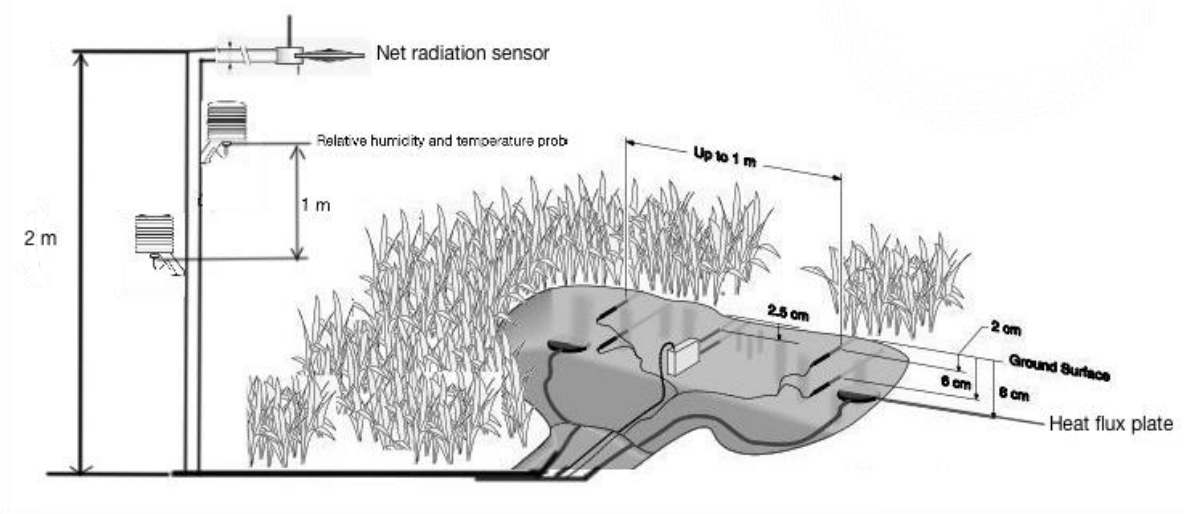

Figure 4.2: Placement of meteorological tower on site.

All the sensors were then connected to datalogger (CR 1000, Campbell Sci). The metrological data were downloaded from the logger upon each visited to the site using Campbell Sci PC200W software.

4.2.2 Study Periods

Data from the two catchments were gathered from 04/03/2013 to 07/08/2014 during which time there were 15 catchment visits.

The meteorological towers were installed within both catchments from 04/03/2013 and have operated ever since; taking measurements hourly. Stream run off samples were taken daily with the exception of the periods from March 2013 to May 2013 and August 2013 to October 2013 when both automatic water samplers were programmed to take samples every two days. Changes of the sampling rate were due to the shooting season meaning a reduced frequency of catchment visits. Unexpected long dry periods and snow periods (October 2013 to March 2014) limited the automatic water sampler performance. In total, there were 130 days of samples from the automatic water sampler for the control catchment and 190 days of sampling for the experimental catchment. In addition to the run off samples, spot samples were taken tracing the top of the gully to the main stream channel on both catchments. Effectively, 8 out of 15 visits to the catchments were chosen to take the spot samples.

4.2.3 Meteorological data

Initially, two micro-meteorological towers were constructed in the experimental and control catchments. During the experimental period hourly recordings were recorded on the tower on the experimental catchment. The tower on the control catchment has also been recording data hourly and was functioning for 291 days out of the 386 days of the total study period. The tower in the control catchment was set to record: temperature, humidity, net radiation and water table. However, the height of meteorological tower in the control catchment and the reflections of the solar panel raised the concerns from the game keeper of the site, and eventually the net radiation and relative humidity probe along with tower above the surface were removed under the request of the land management from 31/7/2013. After this date, only soil temperature, air temperature and water table changes were monitored on the control catchment. The water evaporation was assessed through the meteorological data, where net radiation, relative humidity and soil heat flux, and evaporation were unified by the Bowen ratio (Romano and Giudici, 2009). The energy balance can be written as:

$$\boldsymbol{Rn} = \boldsymbol{\rho\lambda E} + \boldsymbol{H} + \boldsymbol{G} \tag{4.1}$$

With R_n : net radiation (W/m^2), $\rho\lambda E$: latent heat flux (W/m^2), ρ : density of water (kg/m^3), λ: latent heat of evaporation (J/kg), E: evaporation (mm/d), H: sensible heat flux (W/m^2), G: ground heat flux (W/m^2).

The Bowen ration can be written as:

$$\boldsymbol{\beta = \frac{H}{\rho\lambda E} = \gamma \frac{(T2-T1)}{(ea,2 - ea,1)}} \tag{4.2}$$

With β: Bowen ration (-), γ: psychrometric constant (kPa/ °C), T_1: temperature at height z_1 (°C), T_2: temperature at height z_2 (°C), $e_{a,1}$: vapor pressure at height z_1 (kPa), $e_{a,2}$: vapor pressure at height z_2 (kPa).

By unifying equations 4.1 and 4.2, the evaporation can be written as:

$$\boldsymbol{E = \frac{(Rn - G)}{\rho\lambda\,(1+\beta)}} \tag{4.3}$$

To determine the evaporation in this way, it is necessary to measure the temperature and relative humidity (Rh) at least at 2 heights. The relative humidity is determined by the relation:

$$\boldsymbol{Rh = \frac{ea\,(Ta)}{es\,(Ta)}} \tag{4.4}$$

Where $e_{s\,(Ta)}$ is the saturation vapor pressure at the current air temperature T_a.

Saturation vapor pressure (kPa) is a function of the temperature T (°C) and is expressed in the formula:

$$es\,(Ta) \;=\; 0.61\,exp\,(\frac{17.3\,T}{237+T}) \qquad (4.5)$$

Thus, equation 1.3 can be transposed as follow:

$$E = \frac{(Rn - G)}{\rho\lambda \left\{ 1 + \frac{\gamma(T2 - T1)}{0.61h[exp\,(\frac{17.3\,T2}{(237+T2)}) - exp\,(\frac{17.3\,T1}{(237+T1)})]} \right\}} \qquad (4.6)$$

Because of the meteorological tower in the control catchment was taken down during the study, different approaches were used to calculate the water balance from control and experimental data. The evaporation from the experimental catchment was calculated from the Bowen ratio (Equation 4.6). Water balance was set to help elucidate flow pathways especially considering the ephemeral nature of the streams in the study catchments. Lack of evaporation data from the control catchment makes water balance from both incomparable to each other. The water table variances of individual days of both catchments were then used in the later statistical analysis as the water balance variable. The water table was measured in the dipwells using pressure transducers to sense the depth of the water. The transducers were programmed to take measurements hourly. A daily average water depth was then calculated and used in the statistical analysis (referred to as water table from here on). Similar to the events analysis conducted in Chapter 3, the rainfall factor was characterised by its total daily rainfall (referred as total rainfall from here on). The pre-existing moisture condition of the ground on to which any precipitation falls was assessed by the total rainfall 24 hours prior to the start of the daily measurement of rainfall (referred as antecedent rainfall from here on).

4.2.4 Runoff and spot sample data

Two automatic water samples were installed one each on the gullies draining the control

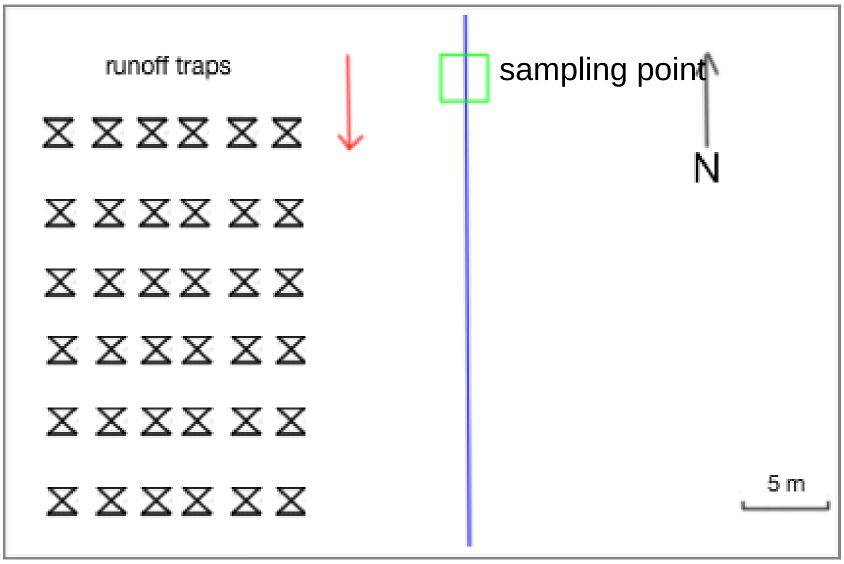

Figure 4.3: the placement of runoff traps in experimental catchment

and experimental catchments. Due to the low occurrence of sampling by the auto-samplers, a program of additional sampling was undertaken. On the basis that water from the study catchments was not leaving via the monitored gullies the water must be draining vertically through the soil profile, we started sampling the spring lines downslope of each study catchment – this resulted in 93 spot samples being taken during the study period. Furthermore, a total of 36 dipwells were installed in the experimental catchment in a transect perpendicular to the natural stream (referred as runoff traps). Two small holes were drilled opposite each other on the side of each trap. The two holes are approximately 30 cm up from the bottom side of the trap. Each runoff trap was placed the position (Figure 4.3) to make the small holes face perpendicular to the stream too. Thus any soil water running perpendicularly towards the stream would have been trapped into the well. Due to the hard sediment rock on both side of the control catchment, the runoff traps were only applied in the experimental catchment.

4.2.5 Sample analysis

The water samples were analyzed in the laboratory for pH, conductivity, absorbance and DOC concentration. The measurement of DOC concentration was by the colorimetric method of Bartlett and Ross (1988). Sample absorbance was measured at 400, 465 and 665 nm using an UV/VIS spectrophotometer. Various studies have demonstrated a strong correlation between absorbance of a sample at 400nm and the concentration of humic matter (Korshin et al., 1997; Bertilsson and Tranvik, 2000). E4/E6 ratio is wildey used as a measure of humification being the ratio of humic acids to fulvic acids (Anderson et al., 1981; Wallage et al., 2006). The E4/E6 ratio was then calculated by using absorbance measurements at 465 and 665 nm of the samples. During the study, the list of analyses was expanded to include anions: fluoride (F), bromide (Br), chloride (Cl), nitrate (NO_3), phosphate (PO) and sulphate (SO_4). The anion data were used in principal component analysis (PCA) techniques to investigate the mixing of different waters in the system and to establish the changes of chemical tracers through the stream thus further indicating the potential changes in flowpaths through the study catchments (Worrall et al., 2003). Anion analysis was performed by ion chromatography (IC). A Metrohm 761 compact-IC to an 813 Compact auto-sampler was used. Standards of 1.25, 2.5, 5 and 10 mg/l were used to create linear calibration curve with samples. Two blank run were used before and after each the standards. An eluent solution of sodium carbonate and sodium hydrogen carbonate were used to maintain a stable baseline.

4.2.6 Statistical analysis

The revegetation effects on DOC concentration and water colour was assessed by relative DOC and relative water colour. Both the relative DOC and relative water colour were calculated as the DOC concentration and water colour from the experimental catchment relative to that in the control catchment for the same month. No water samples or the meteorological data were taken prior to the start of experiment and, therefore, the relative data was not used to assess whether the DOC concentrations or water colour are different between the study catchments but whether the DOC and water colour in the stream runoff in the experimental catchment declines relative to the control catchment with time. Due to the differences between control and experimental catchments, i.e. different dry or wetness conditions of the catchment; different snow melting conditions on different catchments, the auto sampler in experimental catchment was not always collecting runoff samples simultaneously within the control catchment. It was only possible to calculate relative data for 87 days, as a result.

Statistical analysis was applied to the experimental data to assess the benefit of revegetation on DOC or water balance. Two sets of data both include runoff data and meteorological data in statistical analysis, one is based on the DOC variation (Set 1), the other one is based on the relative DOC variation (Set 2). Set 1 data contains the DOC concentration, water colour, pH, conductivity, ion chromatography, antecedent rainfall which was calculated from the previous 24 hours meteorological records, and the water balance of the day. Set 2 data was the relative DOC concentration, month and antecedent rainfall.

Analysis of variances (ANOVA) was applied to the set 1 data to identify the dominant variables in DOC concentration changes in the control and experimental catchments.

Therefore, DOC concentrations from both catchments were assessed with following factors: month, catchment and spot. The month factor have 12 levels representing the 12 months of a year, catchment factor has 2 levels, one for each catchment. Spot factor has two levels, spot sample or not spot sample. Besides the factors applied on the ANOVA, pH, conductivity, antecedent rainfall, evaporation and average temperature of the day were considered as covariates. Set 2 data assessed all stream runoff data from the experimental catchment relative to control catchment over the monthly changes to identify the revegetation effects. An ANOVA was applied on set 2 data with the same factors and covariates used in ANOVA of set 1. In both the ANOVA performed on set 1 and set 2 data, the proportion of variance explained by a factor or covariate was calculated by using the ω^2 method by Vaughan and Corballis (1969), hence any factors or covariates having a probability larger than 95% of not being zero were considered as significant.

Principal component analysis (PCA) was used to understand changes in flow pathways between catchments. The compilation of DOC, water colour, pH and conductivity from set 1 were used in PCA to identify common evolution to stream from soil water. Similar to chapter 3, principal components (PCs) with eigenvalues greater than 1 and the first PC with an eigenvalue smaller than 1 were selected for further inspection. The process of selecting PCs for further inspection is sometime an arbitrary decision (Chatfield and Collins, 1981). The eigenvalue of the correlation matrix which PCA is based on the sum of the diagonal terms, thus the eigenvalue of PCs is equivalent to the number of variables in the original dataset. The rule for choosing PCs can then be explained as the chosen PCs explained more variance than any of the original variables. The parameters applied in PCA all retained different units. Since principal components are calculated from the covariance matrix of the variables, the variables are required to ensure equal weight in the PCA. By *z* transforming all the variables considered in the PCA, all the variables are brought to the same scale (details see chapter 3). As PC scores for one component were plotted against another, the distribution of those score would form clear patterns or easily assessed end-members. The end-members were identified through the plots and the end-member data was reached by comparing scores from the two PCs which formed the plots. The analysis of end-members (EMMA) are commonly used in the analysis of mixing sourced water analysis (Christophersen and Hooper 1992) to help to identify the different source of water. Worrall et al. (2003) illustrated the use of PCA for mixing analysis combined with end-member analysis in an upland peat catchment by comparing samples along potential flow paths from precipitation and ground water, through soil water to streamflow. A further PCA was performed including the anion data. The variables used in PCA were: DOC, water colour, pH and conductivity, water balance; and the anion data from both catchments (Anion PCA). The extension of variables of anion data from set 1 was applied to identify the potential effects of flow path changes, i.e. the dilution from the flow path changes. End-member analysis and ANOVA of PCA was applied to the Anion PCA too. The statistical analysis was to help elucidate flow pathways, especially considering the important ephemeral nature of the streams in the study catchments. The water balance on both the control and experimental catchments should also be included in the previous statistical analysis. After initial assessment of the PCs some were subsequently subjected to an ANOVA following the same methods stated in this section. The principal components applied in ANOVA were the first two components as combined two components usually represented about 50% of the original data variance. The ANOVA was applied on these components to access whether these values vary significantly due to revegetation. The factor included in this ANOVA includes: catchment, month and spot. The covariates in the ANOVA were: pH, conductivity.

4.3. Results and Discussion

4.3.1 DOC concentration

Assessing all stream runoff and spot samples during the experiment periods shows that DOC concentration increased from 31.65 mg C/l to 41.68 mg C/l between control and experimental catchments in all runoff samples (Figure 4.4). Comparisons of DOC concentrations were made between the two catchments in the two different water sample types: stream water runoff collected by auto sampler (referred as runoff) and soil water collected along the stream track (referred to as spot). Results shows that DOC concentration differences between catchments were smaller in spot samples than in runoff samples. The median DOC concentration was 33.65 mg C/l compared to 44.68 mg C/l in runoff samples and median DOC concentration was from 35.60 mg C/l compared to 35.89 mg C/l in spot samples (Figure 4.5). There are two things that should be noted. First, sampling rates of runoff samples in two catchments were different, sampling rates in the experimental catchment were 15.6% higher than in the control catchment. Second, the spot samples were collected on both catchments per visit to the site, and therefore there is a much smaller contrast between sampling rates of the two catchments, with the sampling rate of the experimental catchment was only 3.5% higher than that of control catchment.

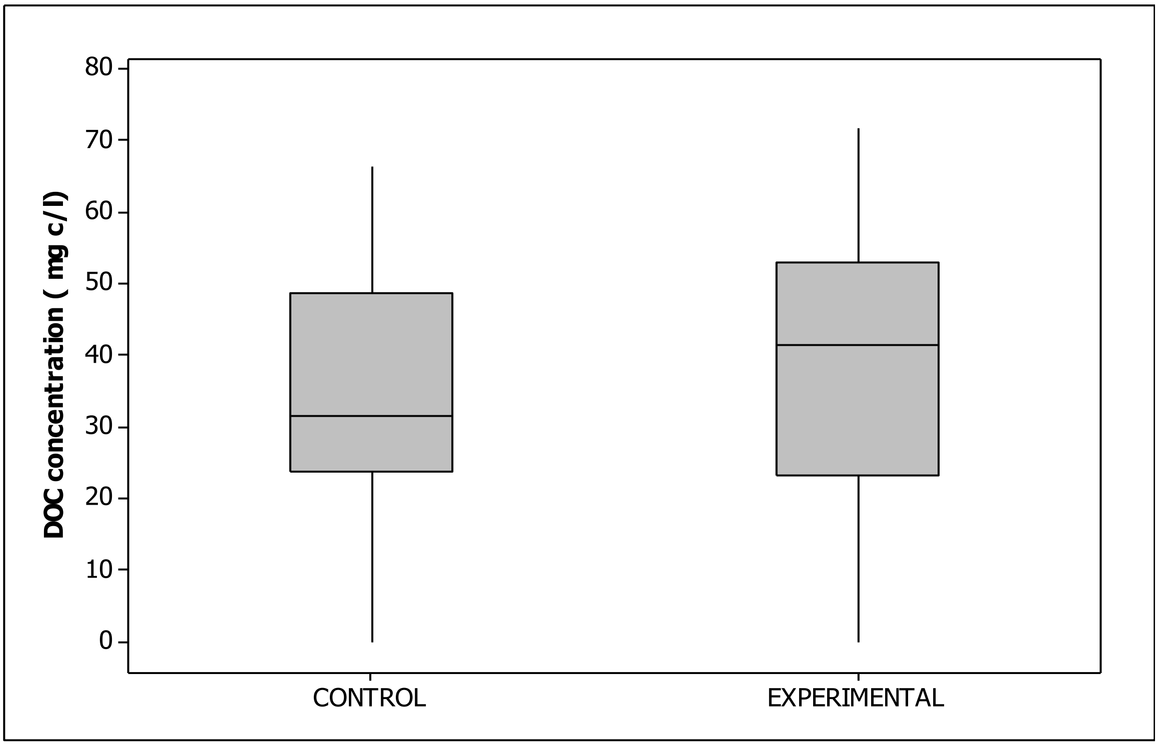

Figure 4.4: Boxplots of DOC concentration in both catchments. The box represents the inter-quartile range; the whiskers represent the range of the data; and the horizontal bar represents the median value.

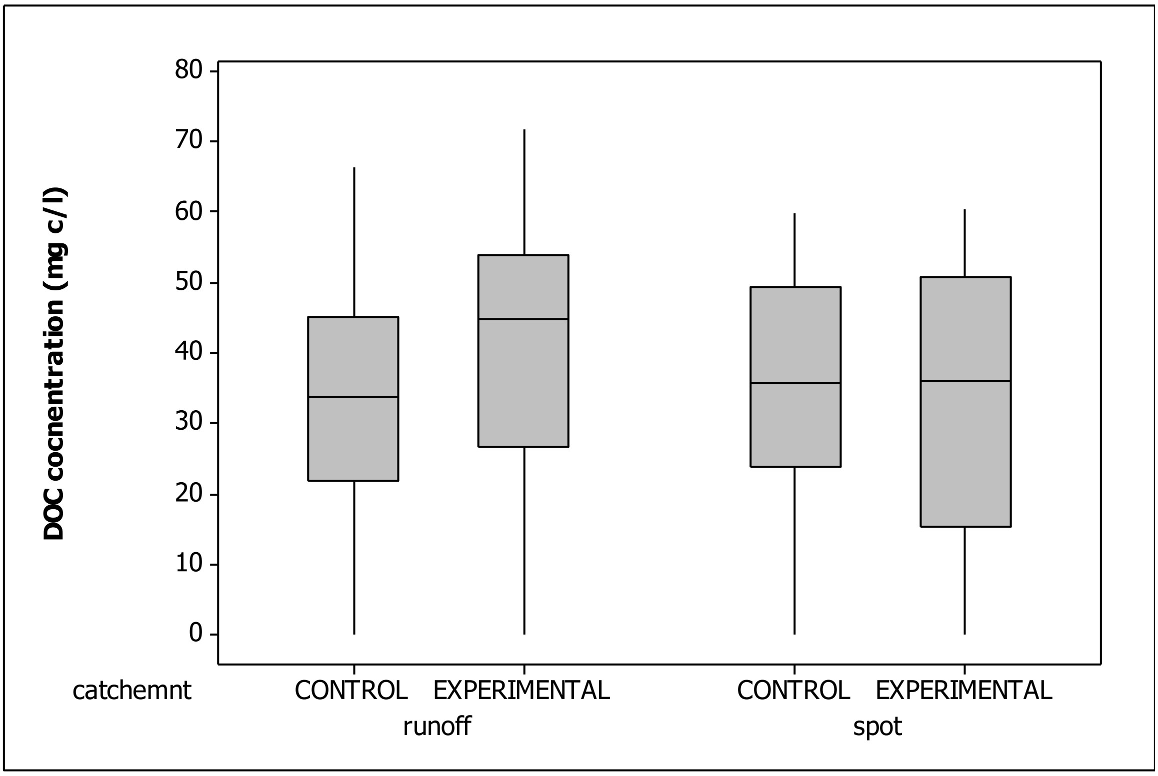

Figure 4.5: DOC concentrations of runoff and spot samples from both catchments.

Analysis of variance (ANOVA) was then performed on DOC concentrations between two catchments. Table 4.1 shows the ANOVA results when set 1 was used as covariates. Results of Table 4.1 show that for set 1 data, only pH, water table changes, and month were significant. In total 9.86% of original variance could be explained by the ANOVA. The Month factor was the most important factor and explained 5.63% of the original variance. Of the covariates, pH explained 2.27% of the original variance while water table changes only explained 1.92% of the original variance.

When anion concentrations (Set 2) were included as covariates in the ANOVA then fluoride, nitrate, and the factor Spot appear as significant. The factors and covariates together explained 10.53% of the original DOC variance. Anion covariates explained 9.32% of variance in the DOC concentration with fluoride explaining 5.84% of the variance and nitrate explaining 3.48% of the variance. Sample type (Spot factor) as a factor only explained 1.16% of DOC concentration variance.

Source	DF	P	Portions
pH	1	0.036	2.27%
water table changes (m)	1	0.013	1.92%
Month	8	0.006	5.63%
Error	219		0.04%
Total	229		
R-Sq = 13.80% R-Sq(adj) = 9.86%			

Table 4.1: ANOVA of DOC concentration using pH and water depth as covariate.

Source	DF	P	Portions
Fluoride (as F)	1	<0.001	5.84%
Nitrate (as N)	1	0.004	3.48%
Sample type	1	0.058	1.16%
Error	198		0.04%
Total	201		
R-Sq = 11.87% R-Sq(adj) = 10.53%			

Table 4.2: ANOVA of DOC concentration using anion concentrations as covariates.

Total rainfall on the day, catchment and spot as factors were not found to be significant when considered in the ANOVA (Table 4.1). The month factor shows that seasonal changes were more influential than other factors. The water table changes, rather than total rainfall of the day, as a significant factor to DOC variance may suggest influences of water balance on DOC concentration. However, whether the water table changes are due to the revegetation is not clear and will be assessed below. The low proportion of the variance explained by the ANOVA (Table 4.1) may be caused by the failure of runoff sampling. i.e. the extreme conditions during the experimental periods caused low sampling rates in both catchments and the auto-samplers would only take samples when peak flow events occurred. The difference between spot and runoff samples is a significant factor, albeit only explaining a small variance in Table 4.2. The significant variances of anion covariates from Table 4.2 may hint at a different source of water or the flow path changes that may contribute to the DOC changes between the two catchments. Further identification of the source of water or flow path changes may require the principal component analysis (PCA) of the available data. The lack of pre-experimental period data means that the analysis should be focused on the DOC concentration changes and water colour changes from experimental catchment relative to control catchment over time.

Overall, the analysis of variances did not observe any direct influence from revegetation upon DOC concentration.

4.3.2 Relative DOC concentration

Relative DOC concentration change did not appear to show an increase or decrease over time (Figure 4.6). In between late winter to early spring (January to March), DOC concentrations increased by an average of 7.8% per month relative to the control. Early winter periods (October to December), however, showed the rise and fall of relative DOC concentration between the three months. There is no clear trend in the relative DOC changes over the months that could be shown in Figure 4.6, as the relative DOC neither increases or decreases over the months. ANOVA was once again applied on the relative DOC concentrations from both catchments. However, none of the factors or covariates were found to be significant in this analysis. This result suggests that revegation was not successful in decreasing the DOC concentration.

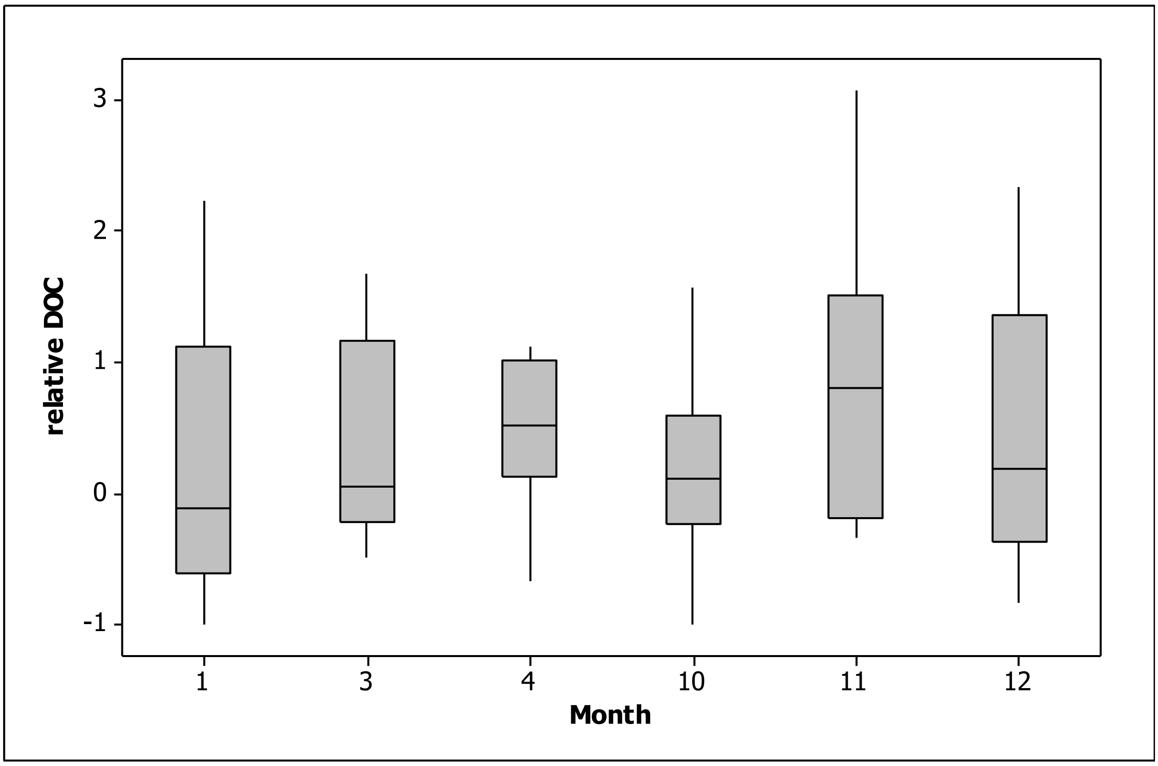

Figure 4.6: Relative DOC concentration changes over months.

4.3.3 Water colour

Water colour of both catchments was measured through the sample absorbance reading at 400 nm and E4/E6 ratios. Boxplots of both absorbance and the E4\E6 ratio show higher water color on samples collected from the experimental catchment than the samples collected from the control catchment (Figures 4.7 and 4.8). The UV-Vis absorbance at 400 nm shows a median value of 0.125 for the control catchment compared to the median value of 0.181 for the experimental catchment. The E4/E6 ratios showed a contrast of ratios from 0.720 to 3.261 moving from control to the experimental catchment. The increases of the absorbance and ratio from control to experimental catchment indicated there are more humic compounds being detected from samples taken from the experimental catchment than from the control catchment. The boxplots of the 400 nm absorbance and the E4/E6 ratios of different sample types at both catchments illustrate the same pattern as the DOC concentration changes shown in Figure 4.5.

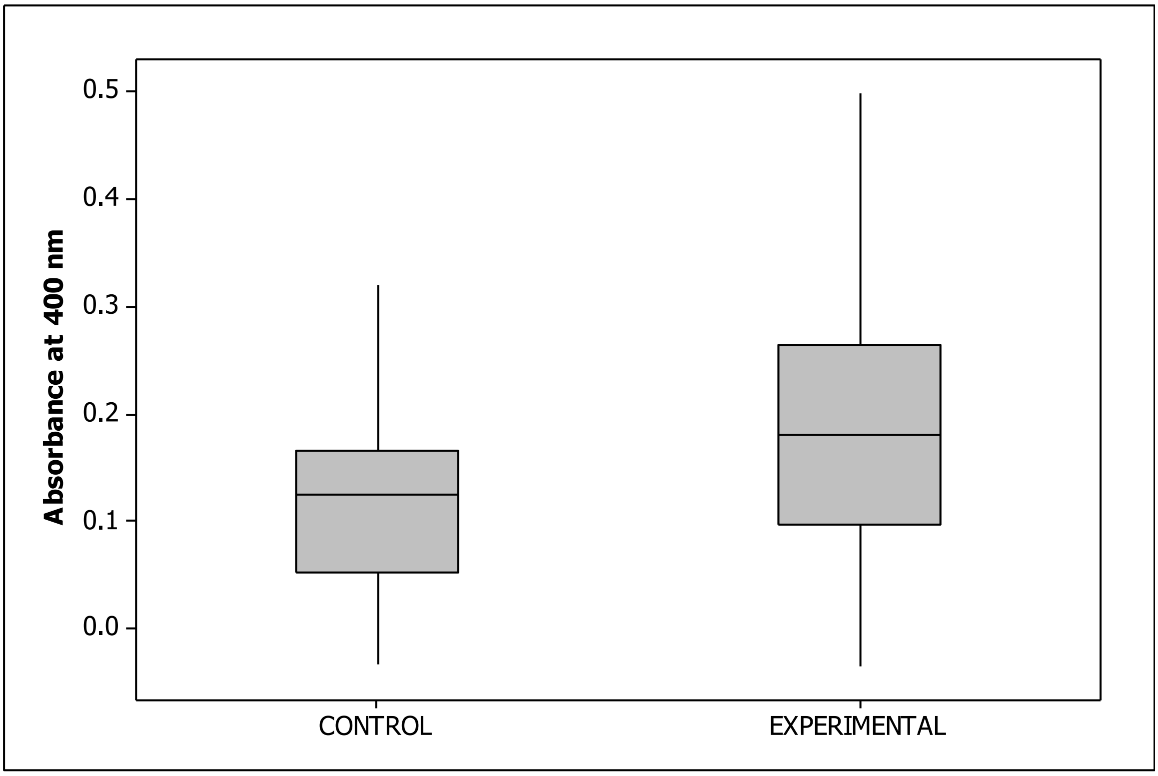

Figure 4.7: Boxplots of sample absorbance at 400 nm of both catchments.

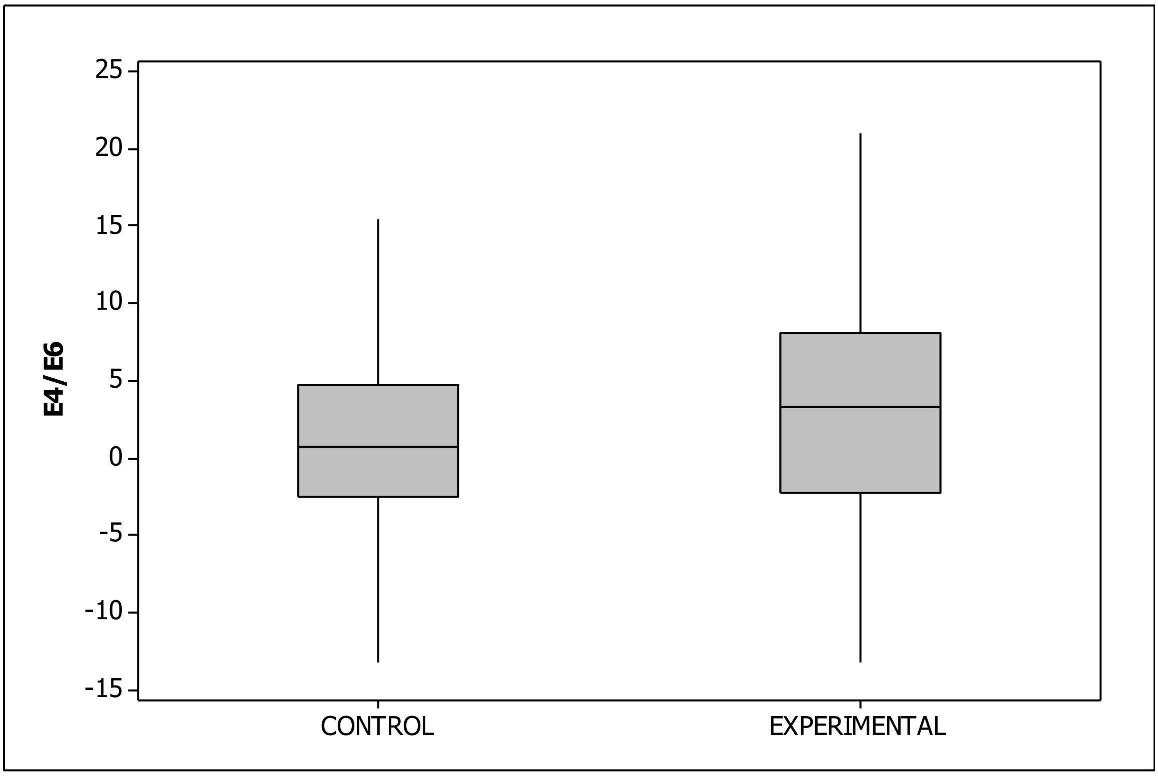

Figure 4.8: Box plots of E4/E6 ratio of both catchments.

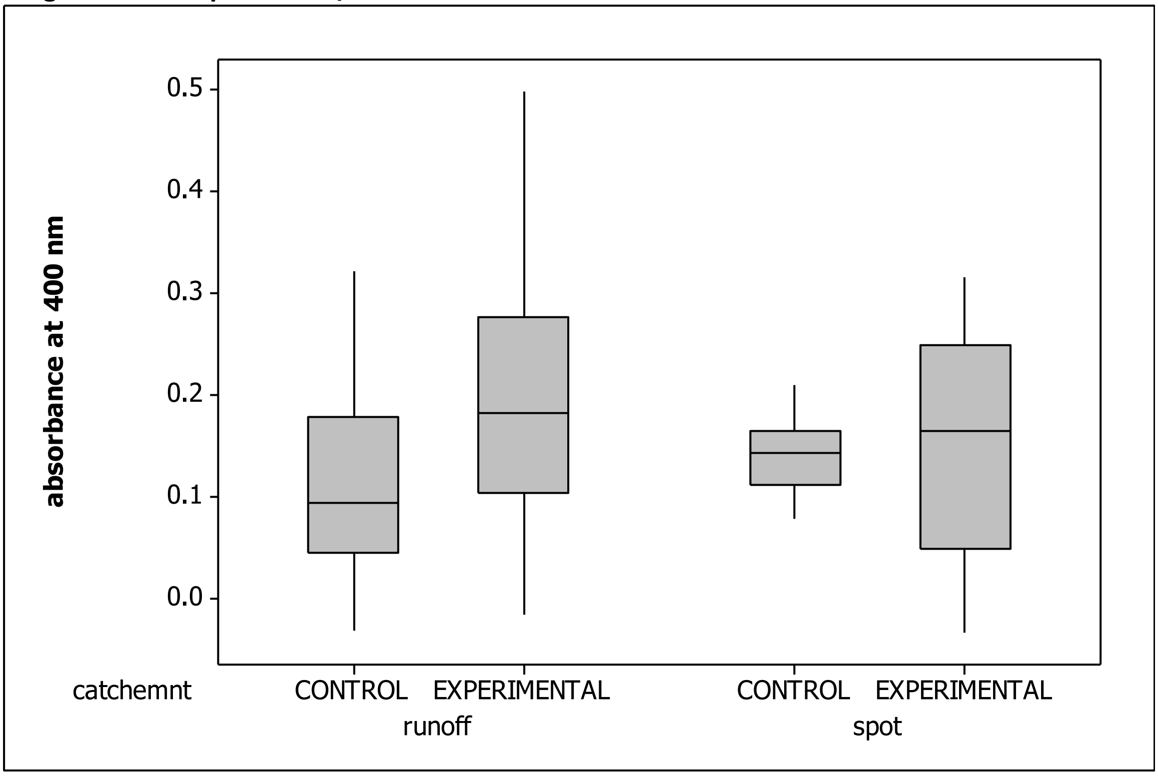

Figure 4.9: Boxplots of spot and runoff sample absorbance at 400 nm of both catchments.

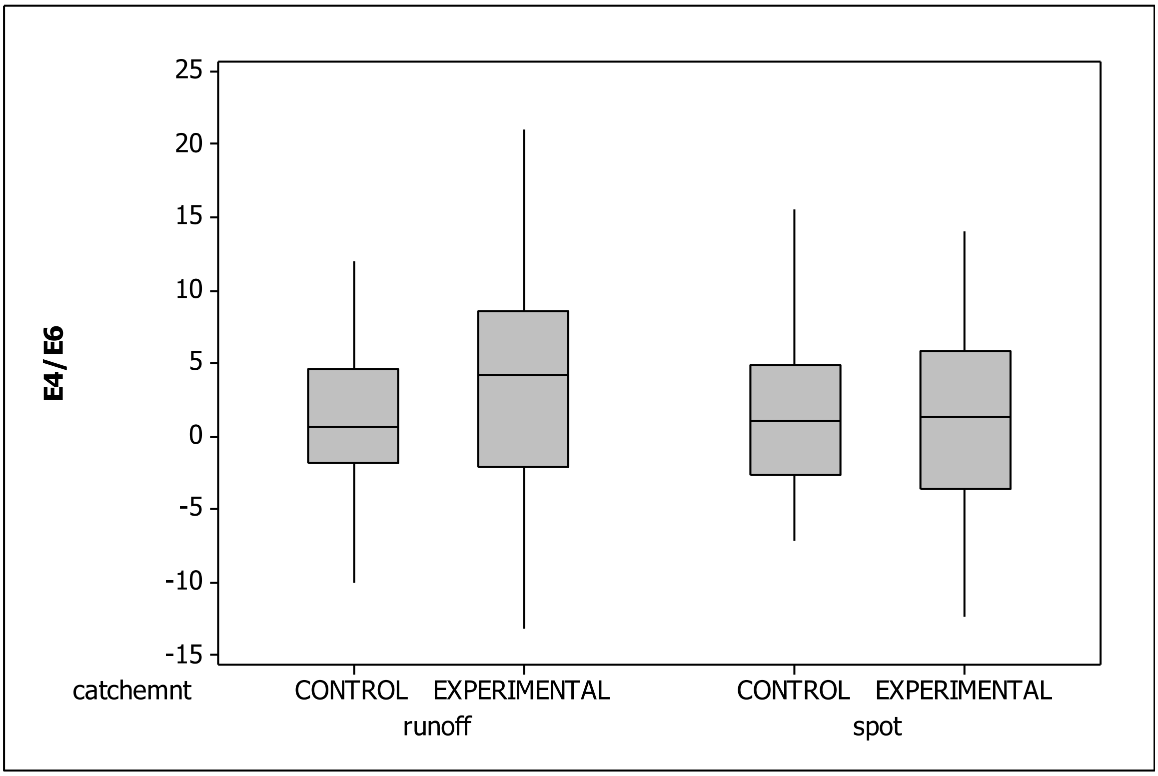

Figure 4.10: E4/E6 of runoff and spot samples from both catchments.

Both the 400 nm absorbance and E4/E6 ratio in runoff samples have larger median values in the experimental catchment than in the control catchment. There was a 92.5% increase on the median values of the concentration in runoff samples from control to experimental catchment, and the median value of E4/E6 ratio in experimental catchment was approximately 5.34 times higher than the value for the control catchment. The changes between catchments on spot samples is much smaller than that seen for the runoff samples, with a 16.2% increase from the control catchment to the experimental catchment on the 400 nm absorbance reading and a 35.2% increase of the same kind in E4/E6 ratios. Following the observation of the DOC concentration changes in section 3.1, the differences of water color between two kinds of water samples may also illustrate the influence of the different sampling rates between two kinds of soil samples. While the runoff sample rates suffered largely by extreme dry or frozen conditions of the land and the failure of the autosamples, the differences of spot sampling rates are relatively smaller than that of runoff samples. Hence, the water color changes between catchment may not be as severe as Figure 4.7 and Figure 4.8 appear to suggest. The further test of influence with this sample type differences on water color could be performed on ANOVAs on the 400 nm absorbance where sample types was used as an factor alongside with other factors such as month, catchment, antecedent rainfall and covariance such as pH, conductivity and anion data. A similar test could also be performed on the E4/E6 ratios too.

Source	DF	P	Portion
pH	1	<0.001	20.22%
Catchment	1	<0.001	7.52%
Sample types	1	0.037	0.01%
Month	9	<0.001	27.02%
Antecedent rainfall	85	<0.001	11.16%
Error	161		0.02%
Total	258		65.96%
S = 0.0603560 R-Sq = 78.81% R-Sq(adj) = 66.04%			

Table 4.3: ANOVA of absorbance (400 nm) when pH and conductivity are applied as covariates.

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Source	DF	P	Portion
pH	1	<0.001	26.67%
Chloride (as Cl)	1	<0.001	6.47%
Nitrate (as N)_1	1	0.002	6.74%
Conductivity	1	<0.001	1.72%
Water table changes (m)	1	0.003	1.99%
Catchment	1	<0.001	9.60%
Sample types	1	0.002	0.02%
Month	9	<0.001	18.36%
Error	166		0.11%
Total	182		
S = 0.0510327 R-Sq = 74.18% R-Sq(adj) = 71.69%			

Table 4.4: ANOVA of absorbance (400 nm) when anion data were included as covariates.

When pH and conductivity were included in the ANOVA of absorbance at 400nm (Table 4.3), the results show all factors included in the ANOVA were significant in explaining the variance of absorbance. Of the two covariates, only pH was found to significant and explained 20.22% of the original variance in the absorbance. Among 4 significant factors, Month explained the most variance in the absorbance changes (27.02%), followed by antecedent rainfall (11.16%) and then catchment (7.52%), and the sample type explained the least variance of the absorbance (0.01%). In total, the factor and covariates explained 66.04% of the original variance in the absorbance data.

In the ANOVA of absorbance at 400 nm with the anion data used as covariates (Table 4.4), month (explained 18.36% variances), catchment (9.6% of the variances) and sample types (0.02%) were found to be the significant factors. Significant covariates were: pH (26.67%), chloride (6.47%), nitrate (6.74%), conductivity (1.72%) and water table changes (1.99%). Variates combined the factors and covariates together explained 71.69% of the variance of the absorbance changes.

Source	DF	P
Water balance	132	0.004
Error	119	
Total	251	
S = 15.8965 R-Sq = 64.06% R-Sq(adj) = 24.20%		

Table 4.5: ANOVA of E4/E6 ratio.

When the same ANOVA was applied to the E4/E6 ratios, the results (Table 4.5) of ANOVA found only water table was the significant factor, contributing 24.2% of the E4/E6 ratio variance.

Results of ANOVA on the absorbance indicates that the seasonal change is the most important factor on the absorbance variance. The catchment was a significant factor indicating that the revegetation effects are the dominant feature between catchment differences. Although the sample types were identified as a significant factor, however the small proportion it contributed to the absorbance indicates the different sample types may not play an important role (Figure 4.9 and 4.10). Antecedent rainfall as a significant covariate disappeared when anion data were included in the ANOVA of absorbance, while the pH was still a significant covariate. The changes of the antecedent rainfall were replaced by various anions. The anion factor combined with the relative high proportion of pH contribution to the whole absorbance variance may indicate changes of flow path or changes in source water mixing.

The ANOVA of E4/E6 ratio also indicated the water table changes were the only factor contributed to the changes in the proportion of humic compounds. As the catchment, sample types and month are all ruled out as potential influences on the humic compound changes, the water table changes therefore may also point to the potential influence of revegetation on the humic compound characteristics.

4.3.4 Relative water colour

The relative water colour was assessed through the samples absorbance at the wavelength of 400 nm for the experimental catchment relative to the control catchment and the E4/E6 ratio of the experimental catchment relative to control catchment over the months (Figures 4.11 and 4.12). Both the relative absorbance (400 nm) and relative E4/E6 ratios showed no clear changes between different months. By comparing the two Figures (Figures 4.11 and 4.12), the observed change in the relative absorbance is reversed when compared to the change in the E4/E6 ratios, i.e., the median relative absorbance changes increased from 0.28 (January) to 3.8 (March) and decreased to 0.12 (April) while the relative ratios was decreased from 0.05 (January) to -4.6 (March) and then increased to 0.014 between January and April. The changes between the months in both Figure 4.11 and Figure 4.12 were also observed to be getting smaller with time. Changes in Figures 4.11 and 4.12 indicate the reverse relationship between the water colour and less humic compounds of the samples collected for the site, i.e. the high water colour observed over months is associated with having less humic compounds in the sample.

ANOVA was used to analyses changes in both relative absorbance (ƛ=400 nm) and relative E4/E6 ratio over the months. Month was used as a factor and antecedent total rainfall was used as covariate in both ANOVA. In the ANOVA of relative absorbance, month was found to be the only significant factor and explained 21.73% variance in the relative absorbance changes. There were no significant factor or covariates found in the ANOVA of the relative E4/E6 ratios. In the ANOVA of the relative absorbance, the monthly changes were not associated with the precipitation as no interaction between Month factor and antecedent rainfall total was observed. In fact, the antecedent rainfall was not found to be a significant covariate at all in both the variance of relative absorbance and relative E4/E6 ratio changes indicates the month factor here in both ANOVA of relative absorbance and relative E4/E6 ratio would represent influence other than that due to precipitation. The seasonal changes observed in both Figures 4.11 and 4.12 may indicate that seasonal variations are a consequence of revegetation. However, the low sampling rates over the several months made the analysis ustruggle to reveal a clear trend of water color changes over experimental periods. In terms of the result of ANOVA of relative E4/E6 ratio changes no factor or covariate was found to be significant, and perhaps associated with the hydrological changes i.e. the flow path changes during the peak flow events.

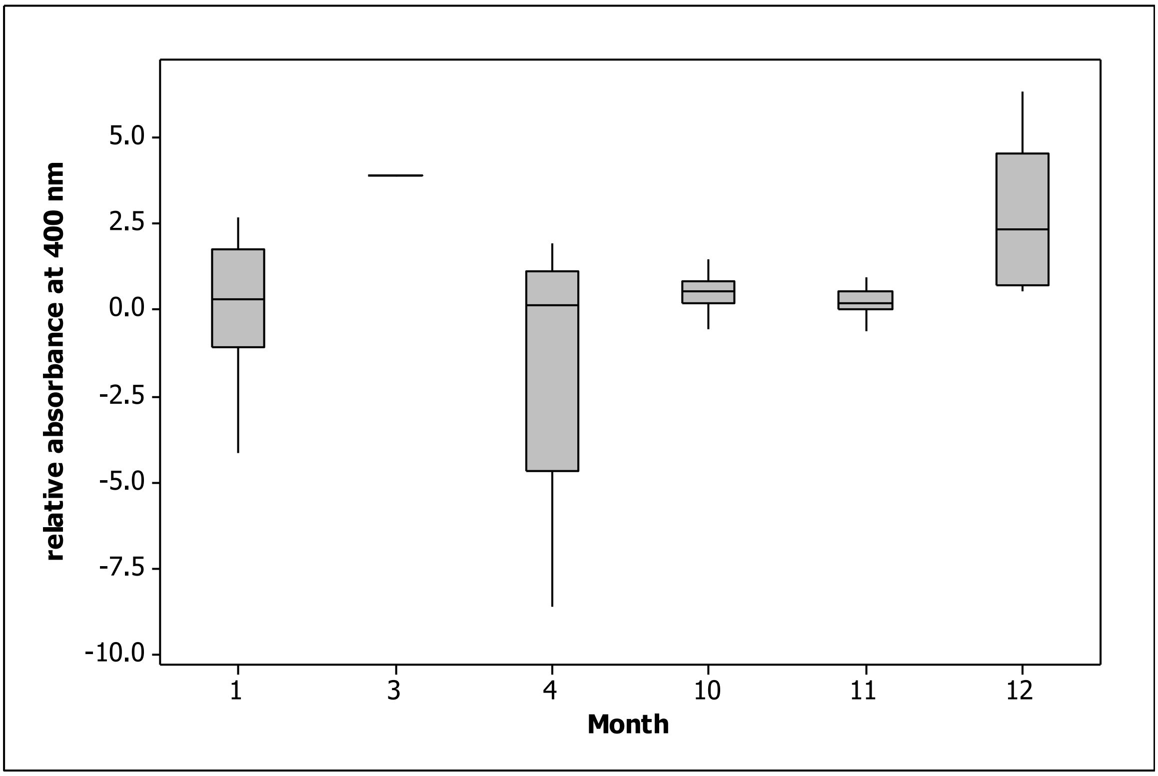

Figure 4.11: relative absorbance at 400 nm over months, where there was only one reading available in March. where 1 stand for Jan, ect.

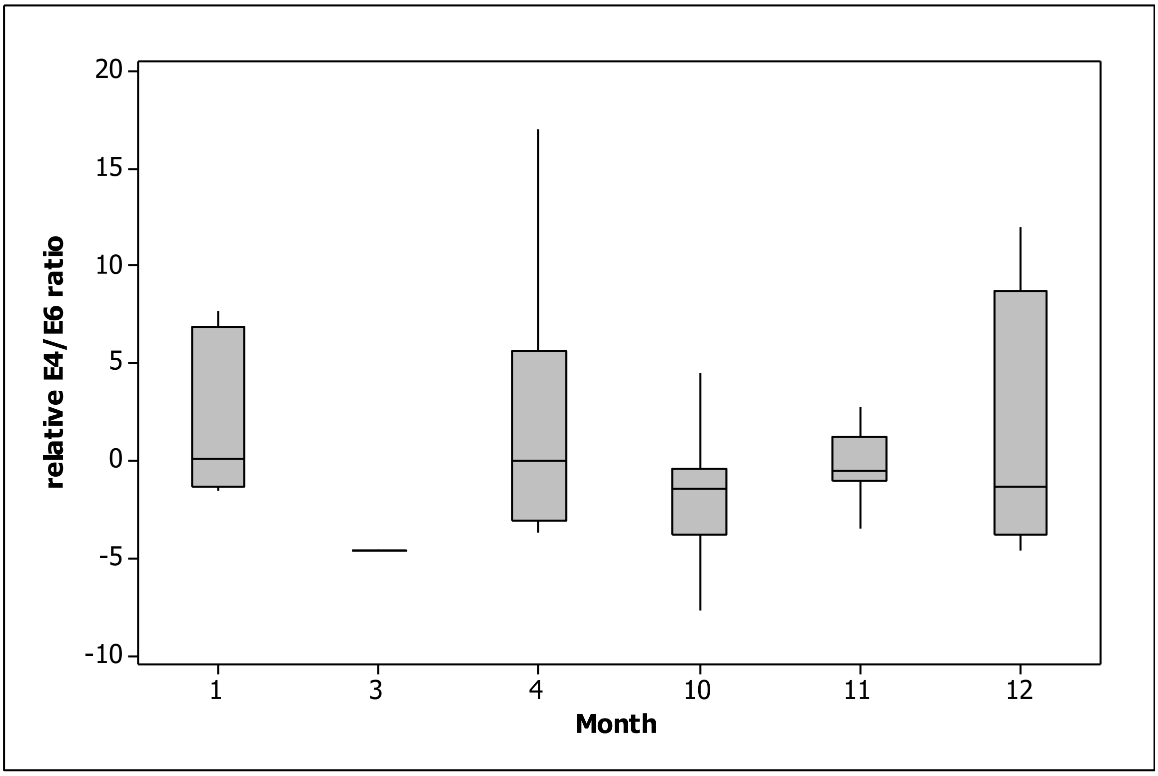

Figure 4.12: Relative E4/E6 ratio over months, where there was only one reading available in March. where 1 stand for Jan, ect.

4.4 Water balance

4.4.1 Water table

Observations of water table depth have been made during the study periods with a total of 715 observations being recorded. In general, the experimental catchment observed a small mean increase of 0.16 m of the daily average water table depth to the control catchment (Figure 4.13) over the study period. An ANOVA was performed on the water table data from the site and it was found that month, catchment and antecedent rainfall total were significant, and together explained 56.81% of the original variance (Table 4.6). The Month factor explained the majority of the variance in the data and the antecedent rainfall total explained the least. There were no significant interactions between the factors. Although the ANOVA indicates the catchment factor as significant and this is manifest as a higher water table in experimental catchment, the impact of catchment was uncertain due to the lack of the pre-vegetation periods data.

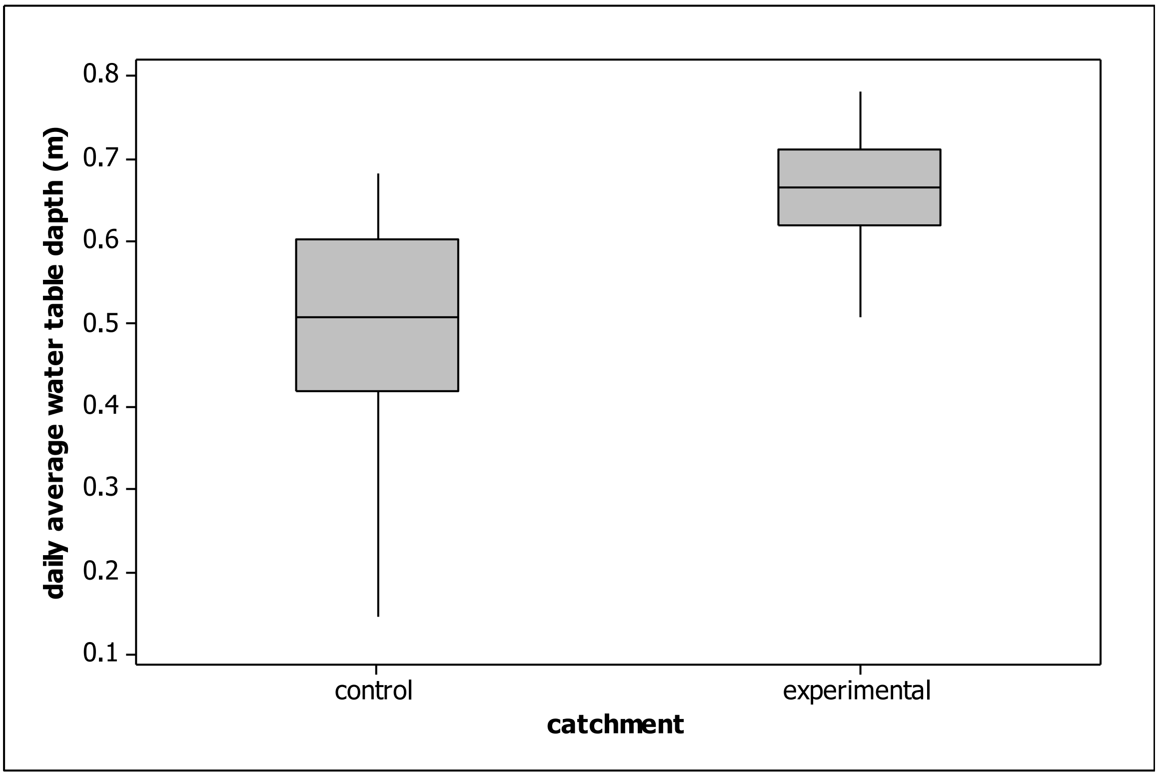

Figure 4.13: Depth of the water table in control and experimental catchment.

Source	DF	P	Portion
catchment	1	<0.001	23.06%
month	11	<0.001	29.56%
Antecedent rainfall	135	0.001	4.16%
Error	567		0.03%
Total	714		
S = 0.104398 R-Sq = 65.70% R-Sq(adj) = 56.81%			

Table 4.6: ANOVA of water table depth for all catchments.

When the water table depth of experimental catchment relative to control catchment was plotted against month then it can be seen the biggest changes were in the spring (February to April).

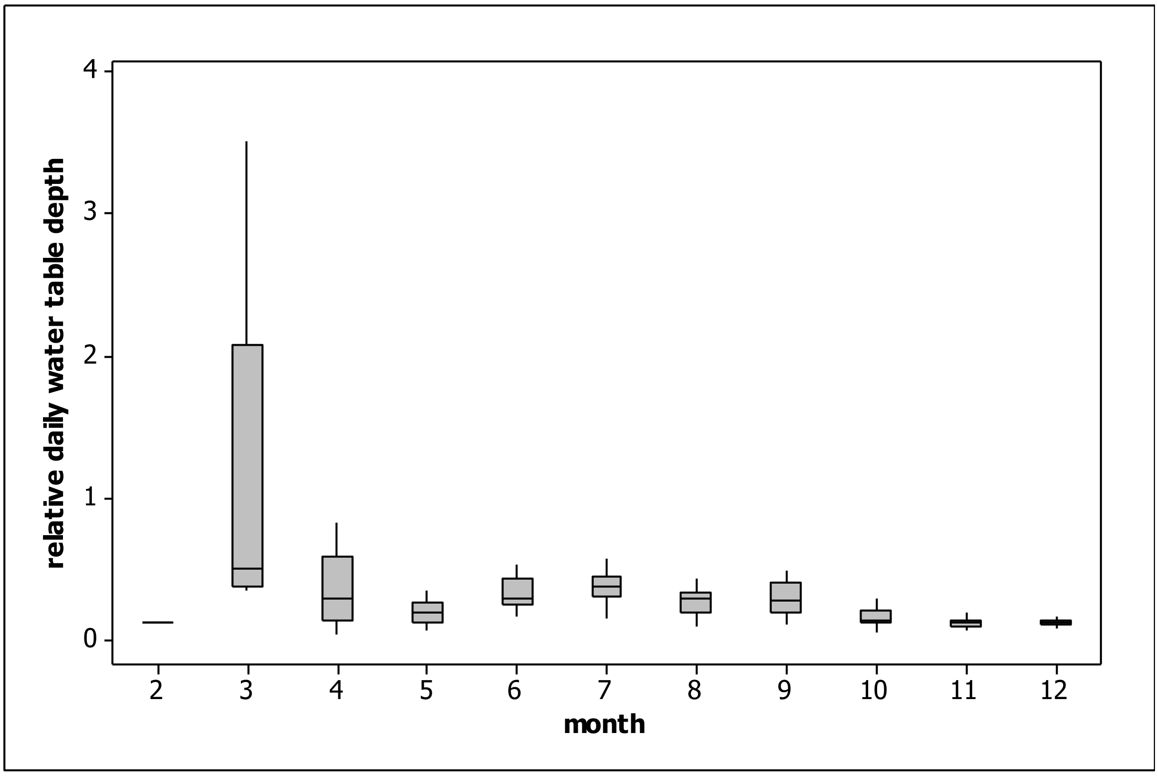

Figure 4.14: relative water table depth over months, where January is marked as month 1 etc.

Relative daily water table depths between the months were observed (Figure 4.14). An ANOVA of relative daily water table found only month as the significant factor at explaining 24.77% of the original variance. The antecedent rainfall was not found to be a significant covariate to the relative water table depth indicating the changes of relative water table depth were not driven by the change of antecedent rainfall.

The analysis of both water table depth in catchments and the relative water table depth indicated the effects of revegetation on maintaining an higher water table depth in the experimental catchment compared to the control catchment.

4.4.2 Evaporation

Since the meteorological tower was taken down at the end of July 2013, the evaporation was calculated based on the experimental catchment. During experimental periods, the experimental catchment observed an average of 6 mm / day evaporation. Figure 4.16 shows the changes of daily evaporation rate over months.

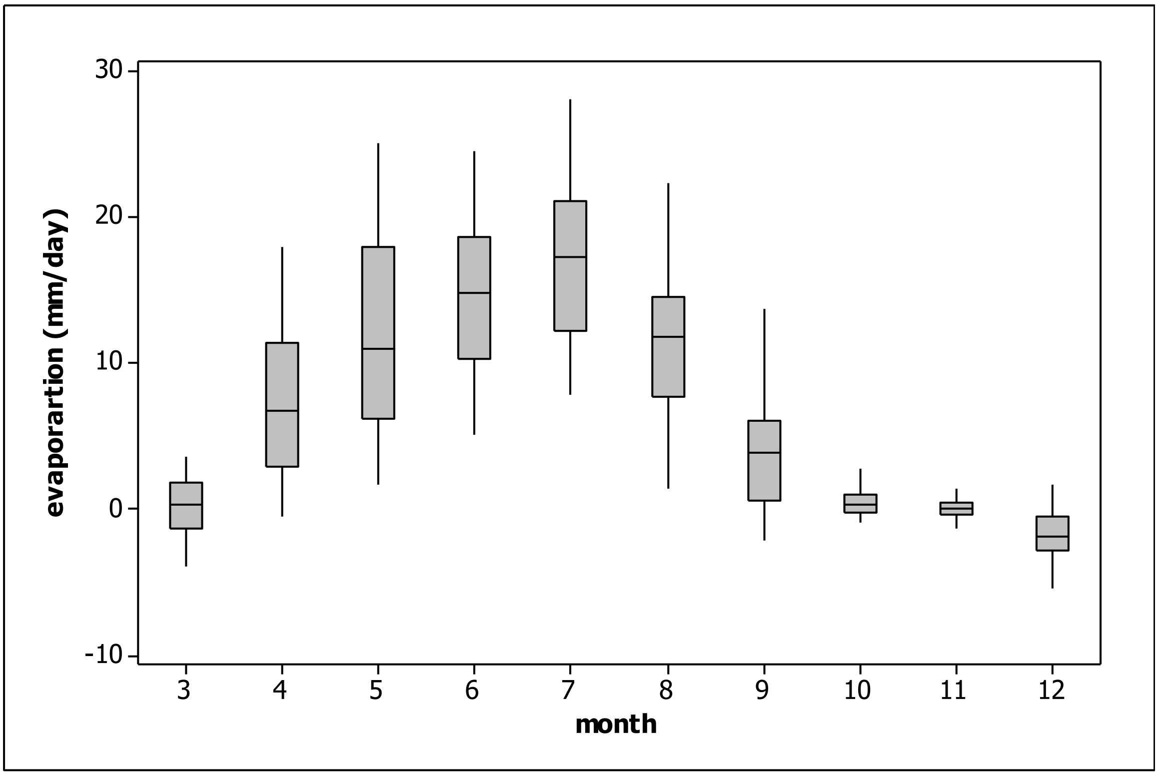

Figure 4.15: Box plots of daily evaporation over months.

Figure 4.15 seems to show seasonal changes over the study periods. The median value of daily evaporation was observed to increase from March (0.24 mm/day) to July (17.27mm/day) and decrease from then to December (1.9 mm/day). Seasonal covariates includes temperature and antecedent daily total daily rainfall as covariates, along with month were used as factor for an ANOVA of daily evaporation. The results of ANOVA (Table 4.7) show month along with temperature explained 56.6% of data variances where temperature as covariates explained 29.56% of the original variance and month as a factor explained 26.95% of the original variance. Antecedent rainfall was not found to be a significant factor. The interaction between month and daily average temperature was also found not to be a significant factor.

Source	DF	P	Portion of variances
Temperature	1	0	29.56%
month	9	0	26.95%
Error	280		1.30%
Total	290		
S = 0.00541073 R-Sq = 58.09% R-Sq(adj) = 56.60%			

Table 4.7: Results of ANOVA of daily evaporation in experimental catchment.

The seasonal changes observed in Figure 4.15 therefore are mainly controlled by changes in the temperature, however, the changes between months are not due to the variations in the antecedent rainfall. A significant month factor above and beyond that explained by significant covariates may indicate changes of vegetation. In Figure 4.16, the spring and summer show a relative low variation of evaporation with a monthly evaporation difference of 40% during autumn and winter season with 190% monthly evaporation change between months. However, the lack of comparison between control and experimental evaporation make the effects of changes of revegetation hard to assess.

4.5 Principal components analysis of DOC

Variable	PC1	PC2	PC3
Z pH	0.544	-0.185	0.063
Z conductivity	-0.21	0.352	0.355
Z DOC	0.429	-0.394	0.203
Z E4/E6	0.038	-0.011	0.901
Z temperature	0.567	0.273	-0.103
Z antecedent rainfall	-0.009	0.602	0.053
z water table changes	0.39	0.499	-0.055
Eigenvalue	1.8518	1.4844	1.0248
Proportion	26.50%	21.20%	14.60%
Cumulative	26.50%	47.70%	62.30%

Table 4.8: First three principal components of PCA .
Where absolute loading values bigger than 0.400 were considered as dominate loadings and marked red.

Principal components analysis (PCA) was applied to understand the mixing of water types and changes in flow path between the study catchments. There were three principal components (PCs) selected during analysis. In total, these three PCs explained 62.3% of variances in the data set (Table 4.8). Among three PCs, PC1 is dominated by significant positive loadings of pH, DOC, and temperature. PC2 has high positive loadings for antecedent rainfall and water table changes. PC3 has very high positive loadings for the E4/E6 ratio which represents the DOC composition changes. From the different dominant loadings of each principal component, PC1 can be seen as the influences of DOC changes with the variances of pH and temperature, PC2 as the influence of hydrological changes, and

PC3 is the change of humic compounds. A comparison of PC1 and PC2 for all sample types is shown below (Figure 4.16).

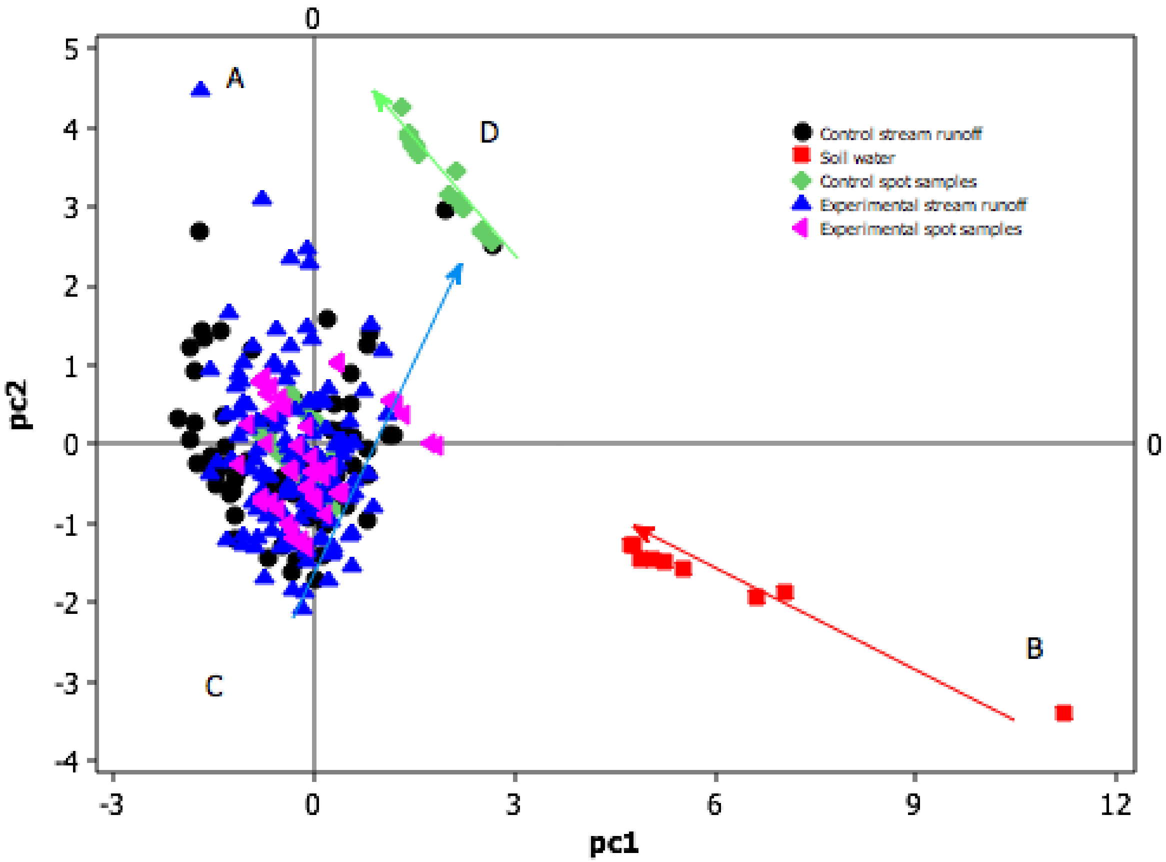

Figure 4.16: A comparison of PC1 and PC2 for all sample types.

The pattern of data suggests that the stream runoff water in both catchments has a common end-member composition (Marked A, Figure 4.16) that in part reflects a dilution trend of soil water samples (Marked B, Red line, Figure 4.16). A series of control spot samples were gathered with events of decreasing DOC concentration and increasing total rainfall could be identified (Marked D, green line, Figure 4.16). This green line is largely made up of samples gathered on 31/07/13, where an event of highest water table changes and high antecedent rainfall compared to other days for the rest of the spot samples was collected. The separation between samples from 31/07/13 and the rest of the samples from both catchments indicates the comparison of high peak flow and low flow events.

The stream runoff water evolves to one of the runoff samples (Marked C, Figure 4.17) with low antecedent rainfall and water table changes. Comparing the two catchments suggests no difference in the mechanism of DOC runoff. A series of ANOVA were chosen to access the early observed different sample rate influence on DOC concentration changes (Section 3.1). Of the three principal components selected, only PC1 and PC3 had high loadings for the DOC concentration. Thus the ANOVA were applied on PC1 and PC3. In the ANOVAs of PC1 were applied on each catchment using sample type (runoff or spot) as factor with pH and conductivity as covariates. In the ANOVA of PC1 in the control catchment, sample type was found to be a significant factor which explained 18.95 of PC1 variance. In the ANOVA of experimental catchment, sample type was also found to be significant factor explaining only 2.12% of the PC1 variance. In the control catchment, DOC concentration of the spot samples (median value of 35.6 mg C g/l in Figure 4.5) are higher than stream runoff samples (Median value of 33.6 mg C g/l in Figure 4.5) but in the experimental catchment the difference is reversed with spot samples having lower DOC concentration (Median value of 35.8 mg C g/l in Figure 4.5) than stream runoff samples (Median value of 44.6 mg C g/l in Figure 4.5). When pH and conductivity were included as covariates in the ANOVA of PC1, sample type was still observed as a significant factor with P value less than 0.001 and explained 25.9% of the original variance in the control catchment, explaining 6.36% of the original variance. ANOVA of PC1 for the two catchments comparing their respective stream runoff and spot samples shows that there was a significant interaction with the difference between stream runoff and spot samples being different between the experimental and control catchment. However, for the ANOVA of PC3, which stands for the water colour changes, the sample type was not a significant factor in either of the catchments. The changes of the water colour were not due to the interaction with the difference between sample type being different in the two catchments indicating possible DOC composition changes or flow path changes.

4.6 Principal components analysis including anion data

The PCA of the DOC, water colour, antecedent rainfall, water table changes, pH and conductivity give different features when the anion data from both catchments were included. There were 6 anion variates included in the PCA. There were fluoride, chloride, nitrate, sulphate, and nitrite. All the variates have been z transformed. There were four principal components chosen from the PCA (Table 4.9) and these 4 PCs explained 65.6% of variance of the data included in the analysis. Among the four PCs, the first component (PC1) and second component (PC2) together explained about half of the original variance in the data (44.6%). First principal component (PC1) is dominated by the positive loadings of nitrite (loading of 0.437) and nitrate (loading of 0.450), second principal component is dominated by negative loading for chloride (loading s of -0.572) and conductivity (loading of -0.60). Third principal components have the distinct loading for nitrate (negative loading of -0.43) and pH (positive loading of 0.554). Unlike the first three principal components that were dominated by variation in anion concentrations, the fourth principal component (PC4) was dominated by variation in DOC (loading of 0.612) and fluoride (loading of 0.592).

Variable	PC1	PC2	PC3	PC4
Z Fluoride (as F)	0.166	-0.145	-0.116	0.592
Z Chloride (as Cl)	0.222	-0.572	0.018	-0.085
Z Nitrate (as N)	0.361	0.046	-0.430	-0.193
Z Sulphate (as S)	0.424	-0.223	0.062	0.019
Z Nitrate (as NO_2^-)	0.437	0.282	-0.153	-0.166
Z Nitrate (as NO_3^-)	0.450	0.259	-0.193	-0.172
Z pH	0.227	-0.020	0.554	0.059
Z Conductivity	0.106	-0.600	-0.085	-0.020
Z DOC	0.035	0.021	-0.403	0.612
Z E4/E6	-0.006	0.036	-0.049	-0.015
Z PTemp_C_Avg	0.253	0.227	0.403	0.270
Z Antecedent rainfell	0.146	-0.173	0.156	-0.205
Z water table changes	0.262	0.097	0.267	0.231
Proportion	27.70%	16.90%	11.30%	9.70%
Cumulative	27.70%	44.60%	55.90%	65.60%

Table 4.9: First four principal components selected by PCA including anion data. Where absolute loading values bigger than 0.400 were considered as dominate loadings and marked red.

The pattern of Figure 4.18 and its end-members (E-F-G) are quite distinct from that of Figure 4.17. Plot of PC1 against PC2 in PCA including anion data (Figure 4.17) suggests that the runoff water and spot samples in both catchments are sourced from a common end-member (Marked E in Figure 4.17). The majority of samples from the experimental catchment appear to evolve in two opposite directions (Marked F and G in Figure 4.17) which dominated by stream runoff and spot samples respectively. Stream runoff of experimental catchment evolves from samples composted by low concentrations of nitrite, nitrate, chloride and low conductivity to samples containing high concentrations nitrite, nitrate, conductivity and chloride. Compared to runoff samples from the experimental catchment, spot samples are changing from the same composition of low nitrite, nitrate, chloride concentration and low conductivity to the high nitrite, nitrate concentration but lower conductivity and chloride composition. Comparing control to experimental catchments indicates no clear compositional changes of the samples. Two sets of ANOVAs were applied on first two principal components (PC1 and PC2).

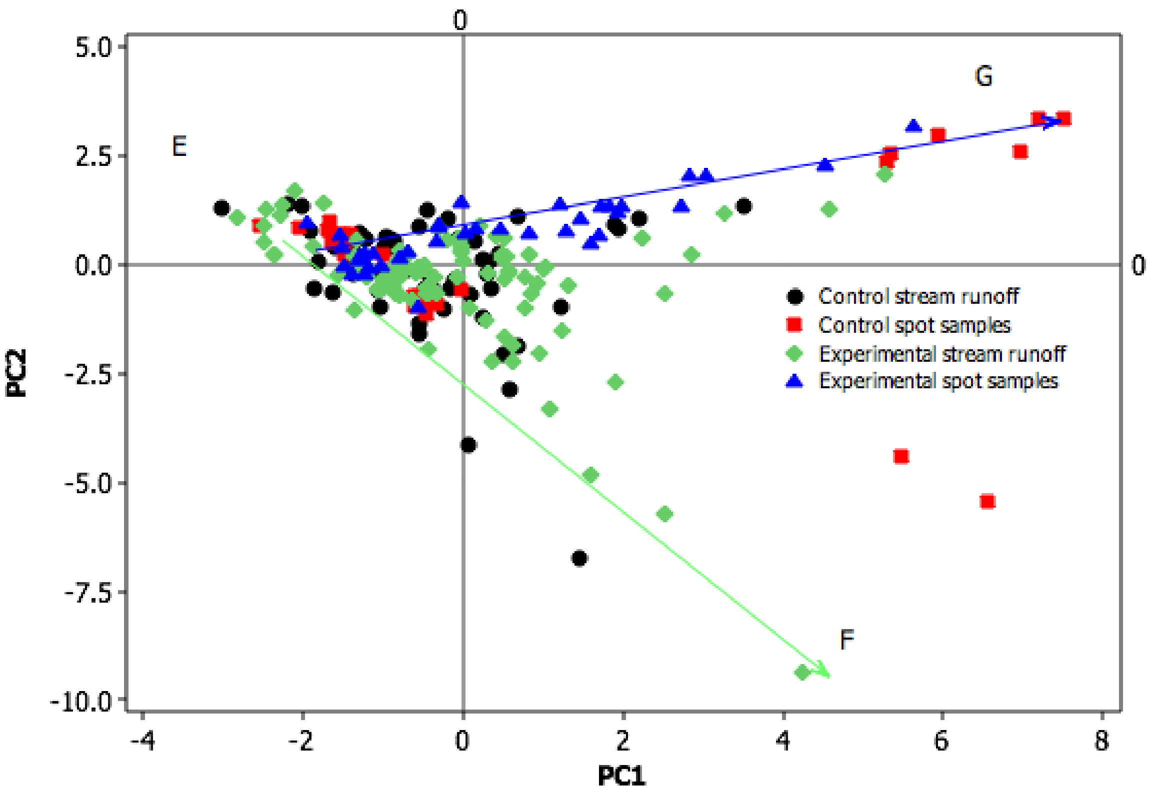

Figure 4.17: A comparison of PC1 and PC2 for all sample types based on anion data.

Results of two sets of ANOVA using sample type (stream runoff and spot samples) as a factor between the two catchments respectively suggesting that the difference between samples types in the control catchment was not significant for either PCs while the sample type was a significant factor ($p<0.001$) for PC2 (the factor explained 11.9% of variance of PC2) but not a significant factor for PC1 in the experimental catchment. As the difference of sample type reflects mainly in the different sampling rates, the different pattern (line EG and EF in Figure 4.17) indicate the soil runoff water suffered by the change of severe weather condition dominated sample rate variances and thus concentration changes of nitrate and nitrite (Pattern of EF) were linked to the experimental runoff samples. The trend E-G linked concentration changes of chloride and change of conductivity to experimental spot sample sampling rates which are less affected by weather conditions. Therefore, the pattern changes on Figure 4.17 reflect the composition changes of water samples. Beside PC1 and PC2 in the PCA of anions (Table 4.9), the fourth principal component (PC4) is the only component dominated by the loading of the DOC concentration (positive loading of 0.621 in Table 4.9). As all first three components represent one composition combination of data set 2 been analyzed, each of three components is plotted against the PC 4 to identify the possible relationship between DOC and each composition albeit PC4 only represents 9.75% of variance of data.

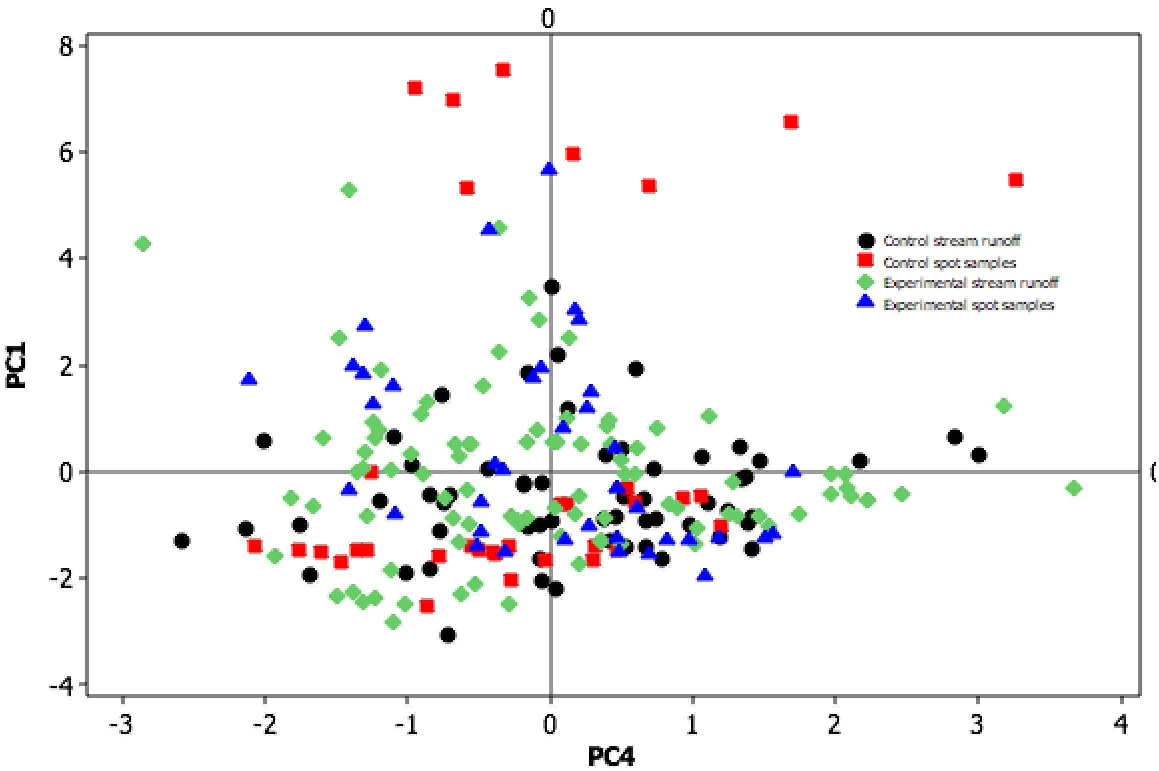

Figure 4.18: A comparison of PC1 and PC4 of all sample types based on anion data.

A mix of all type of samples in both catchments of Figure 4.18 suggests no DOC composition changes on nitrite and nitrate level at all types water of both catchments albeit there is a clear separation of control spot samples (Red dots of Figure 4.18). The control spot samples towards the negative end of PC1 on Figure 4.18 were from the 31/07/13 which has already been identified above as an event marked out by the high antecedent rainfall. The separation of control spot sample is most likely to be caused by the hydrological difference between the days upon which spot samples were taken. The apparent difference in the variance of the spot samples with respect to nitrite and nitrate composition from the two catchments may be caused by the catchment difference, but may primarily suggest the experimental spot sample are less sensitive to the hydrological change. Patterns visible in Figure 4.19 suggested the spot samples' DOC is less variable with respect to conductivity and chloride, whereas the runoff samples' DOC is more variable with changes in conductivity and chloride. In fact, the decrease of DOC on Figure 4.19 (Marked Green and Red lines) comes with the rapid changes of conductivity and chloride. Figure 4.20 shows the variance of pH and nitrate of samples from control catchment while the spot samples and runoff samples of the experimental catchment evolve to the opposite end of the pH and nitrate variance.

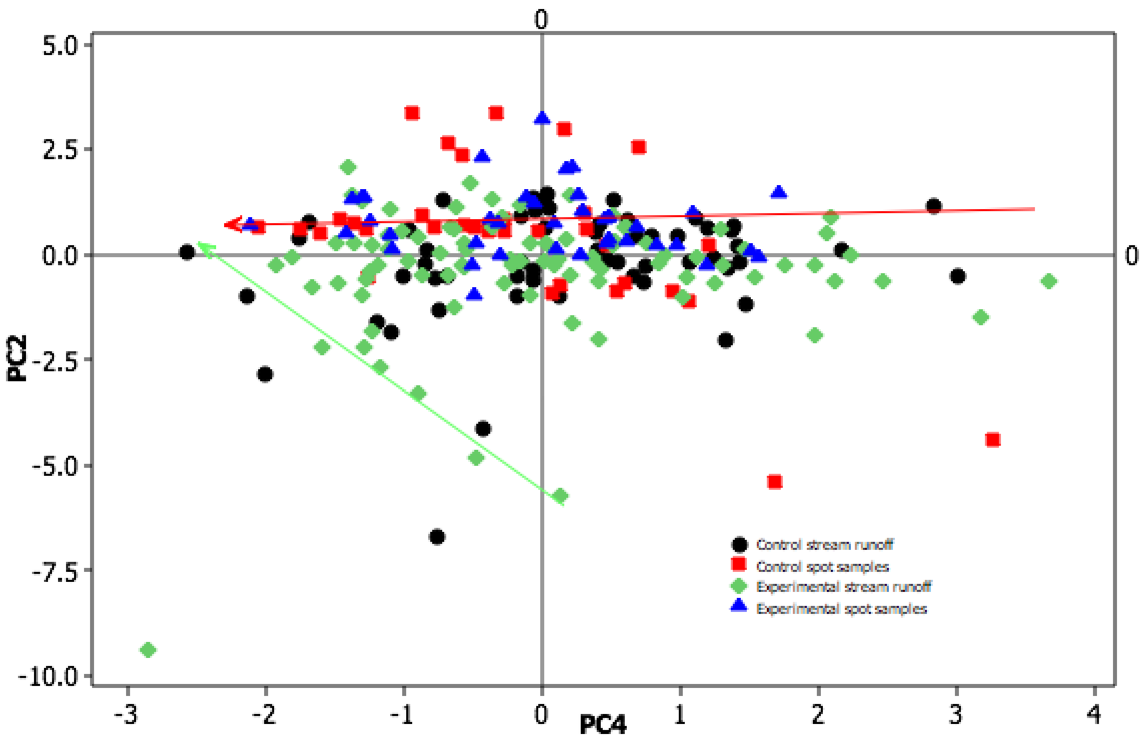

Figure 4.19: A comparison of PC2 and PC4 of all sample types based on data set 2.

Comparisons of all three plots (Figures 4.18 to 4.20) suggest the DOC composition changes between catchments. The runoff samples and upper stream DOC composition are associated with the variances of nitrite, nitrate, conductivity and chloride. The control catchment DOC is less altered by the variance of pH and nitrate, but the experimental catchment DOC varies with the changes of pH and nitrate. The analysis of PC1 vs PC2 have illustrated the DOC removal on the experimental catchment, the analysis of DOC compositions here further indicates the removal of DOC may be due to flow path changes.

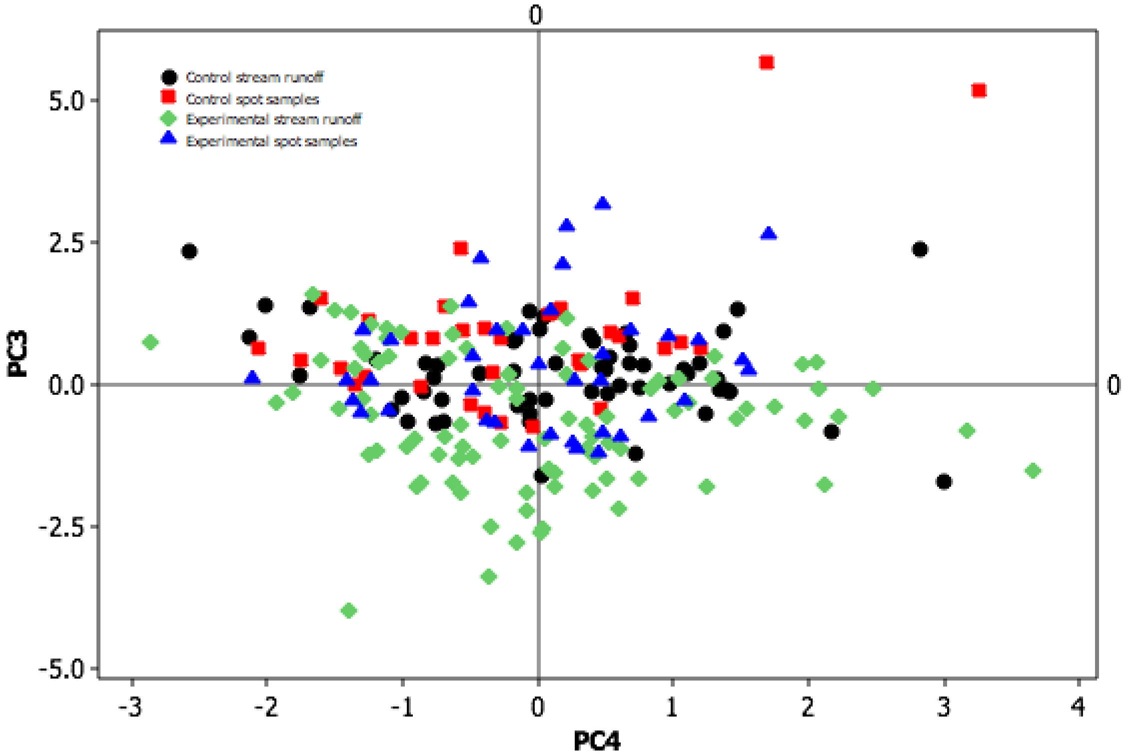

Figure 4.20: A comparison of PC3 and PC4 of all sample types based on data set 2.

The relative DOC changes of an earlier study contradict with the PCA results, where no linear relationship of relative DOC between months was observed. The observation of the relative DOC leads to the assumption that DOC removal observed may not be because of the revegetation. However, results of the relative water table changes over the months suggest that the revegetation indeed leads to the stable water table. It should be noted that the lack of comparable data across different months leads to the separation in Figure 4.12 to form 2 sections with spring and winter. The noticeable stable relative water table may just reflect the frozen water table during low temperature and thereby the DOC changes would most unlikely be effected by the revegetation. Result of an ANOVA of water table changes among all catchments where month, rainfall as covariates and catchment as factor find apart covariance of rainfall, difference between catchments is a significant factor of water table variances (two variates made up 30% of variance of the water table changes).

4.7. Conclusions

No clear impact of revegetation upon DOC changes was observed during the research period. The study found the median DOC concentration was 41.7 mg C g/l in the experimental catchment and 31.7 mg C g/l in control catchment. There is no clear trend of the relative DOC concentration changes over the month despite the different sampling rates between runoff sample and spot sample. A clear seasonal pattern in the relative water colour changes were observed and interpreted as associated with revegetation. However, the experimental catchment observed high water color less humic water sample and control catchment observed low water color and more humic samples.

Although the revegetation found no impact on DOC changes, revegetation shows a significant impact on the water table changes. A noticeable 32.9% of relative water table variances were observed in spring season. The experimental catchment maintained a 0.16 m higher water table depth than the experimental catchment.

Chapter 5 Column study on bank filtration

5.1 Introduction

The majority of the drinking water supply for the northern England is sourced from upland peat leading to localised DOC-water colour problems for water treatment. Early chapters discussed the land management and in particular drain blocking effects upon DOC release from peat. After three years of experiments based on field studies, drain blocking was found to be a somewhat effective control of DOC export from peat, but may not act as an efficient management system to limit DOC release into surface waters of catchments. Besides the land management, various studies have drawn attention to other possible drivers of DOC export. For instance, specific hydrological conditions, i.e. storm flow, as these conditions would act as the main contributor to DOC export. Chapter 3 examined the effects of hydrological changes upon the DOC export specifically the effect on peak flow events, The results of studying peak flow events suggested that during peak flood events the flush of water brought more DOC to the main stream channel despite the drain blocking. As the most of the DOC export was due to the rapid short term hydrological changes, drain blocking was not the most ideal management for DOC removal.

Alternatively, different soil-water interactions, especially in the near stream river aquifer system could remove DOC from water. Several researchers (Maeng et al., 2011; Derx et al., 2014) have shown that the DOC removal along a flowpath in an aquifer is a complicated process that can be caused by biodegradation, adsorption of soil or a combined process of both biodegradation and adsorption. The physical adsorption of DOC has been widely observed in various different soil types (Kortelacien et al., 2006; Essandoh et al., 2013).

Sandy soils have been shown to have the greatest removal rate while clay soils seem least likely to adsorb DOC (Essandoh et al., 2013). In well drained organo mineral soils, low flow through the lower mineral layer acts to absorb DOC, and as a result, DOC is retained in the upper organic. The DOC concentrations in streams draining organo-mineral soils typically show increasing DOC concentrations with increases in flow as flow comes from the organic layers and not the mineral horizon (Clark et al., 2008). Increased soil acidity has been shown to increase DOC adsorption in mineral soils (Kerr and Eimers, 2012; Chapman et al., 2008). As soils recover from acidification, DOC adsorption by soil would decrease and in turn soil water DOC would increase (Kew and Eimers, 2012). Besides soil acidity and flow path changes, soil temperature and DOC adsorption show a positive relationship with increased concentration of DOC present at high temperatures (Kaiser et al., 2001). Therefore, the adsorption of DOC through soils is controlled by the flow path changes in-between different soil layers and the soil acidity and hydrological conductivity changes. Study conducted by Essandoh et al. (2013) on aquifer soils observed the relatively lower DOC removal rate in surface soils compared to pure sandy soil systems. Although the surface soil shows the relative lower DOC removal rate, Essandoh et al. (2013) observed the active microbial activity in the first few centimeters near the surface leads to DOC degradation. Conversely, Cha et al. (2005) suggested that the depth of the soil in the unsaturated zone have no direct link to the DOC removal. Essandoh et al. (2013) illustrated, using a column study, that longer travel distances of elution water in the unsaturated zone would enhance DOC removal. Given the potential for DOC removal in aquifers and sub-soils there have been attempts to use this approach to remove DOC at the water supply scale. River bank filtration (RBF) has driven interests worldwide as it is used as the main water treatment for DOC in the city of Berlin, Germany and pre-treatment in various other countries (Ludwig et al., 1997; Ransch et al., 2005). Therefore, this chapter will discuss the DOC dynamics in aquifers rather than the peat soil, as RBF may provide a new method of DOC control for the UK.

In the case of Berlin, use of RBF meant avoiding adding chlorine to the raw water and reduced the cost at the conventional drinking water treatment. Numerical studies showed that, the RBF efficiently removed the bulk of the dissolved organic carbon. The removal of DOC especially biodegradable fractions of DOC, is essential to RBF as the use of RBF raised concerns that RBF would lead river bed clogging, and therefore introducing more persistent pollutants through filtration (Grünheid et al., 2005).

Several studies have been conducted on the removal of DOC through bank filtration (Miettinen et al., 1994; Grünheid et al., 2005). Kinetic properties like water quality going through the system (e.g. biodegradation), residence time and travel distance (Grünheid et al., 2005) would largely effect the process of changing from oxic to anoxic/anaerobic conditions during bank filtration and therefore effects the DOC degradation through the filtration process. Miettinen et al. (1994) and Schofrnheinz et al. (2003) showed that retention time and temperature are the key factors in the degradation of the DOC.

Retention times used for bank filtration vary widely because of the different approaches to the design of bank filtration. In Berlin, bank filtration is used as the main water treatment aiming to remove most of the biodegradable dissolved organic carbon (BDOC), pathogens, and degradable trace organic pollutions from the surface water. In North America, bank filtration is used as the pre-water treatment primarily to remove the pathogenic microbes, turbidity and some dissolved organic carbons (DOC). Two approaches from EU and North America lead to the different designs of the treatment, most noticeably, treatment retention time. Bank filtration in the EU has the longer retention time, normally lasting from weeks to months, while North America has much shorter retention times only lasting several hours to days (Grünheid et al., 2005). Berlins' system uses a semi-closed underground water system which has its unique soil and water cycles characteristics. Therefore, DOC removal by the Berlin water treatment system using bank filtration may not be suitable for other environments. Besides the site limitations that may affect the bank filtration impact on removing DOC from surface water, different DOC fractions would also control the different DOC removal rates. Dunnivant et al. (1992), observed the breakthrough of naturally occurring DOC from soil columns concomitant with, or significantly after, the solution of conservative tracers, and the movement of the DOC through the soil column was effectively described by chemical adsorption processes. Essandoh et al. (2013) also indicated that the longer retention time and longer travel distance would largely enhance the DOC in the removal process in the unsaturated zone of aquifer. Kalbitz et al. (2004) found that concentration of DOC in deep soil horizon and its export from mineral subsoil is usually small with sorptive stabilization of DOC the likely main process for retention. Therefore, in this study laboratory column experiments were used to mimic the study of DOC adsorption by aquifer recharge on a river bank. Most of the column studies (e.g. Jardine et al., 1992; Essandoh et al., 2013) on the column imitation of DOC changes also considered the different DOC effluent concentrations as the higher effluent concentration showed better removed rates. The characteristics of the aquifer sediment; redox conditions; and the composition of the DOC may also play important roles that control the effectiveness of bank filtration, and with respect to this study, the hydrological transport of DOC from peat soil may differ from that in the organo-mineral soils that have dominated previous studies. The risk of artefacts in the type of lab experiment (column study): the use of sieved soil instead of intact soil core might have changed the mobilisation and leaching of DOC, however, when both sieved soil and intact soil core were used in experiment, the pattern of DOC leaching was similar (Anderson et al., 1999). The experiment was set to identify the changes of the DOC concentration changes by mimicking the bank filtration process through a column study.

5.2 Materials and methodologies

5.2.1 Elution Water

Water containing DOC was collected from a stream channel located at Moor House, Durham. This site and the characteristics of DOC are described by Moody et al. (2013). Water was collected in 1 litre polyethylene bottles and immediately transported to the laboratory and stored at 4 ^{o}C until use. The DOC concentration of this stock solution was increased by evaporation with 2 litters of sample left in an oven of 80 C^{o} for 24 hours to bring down the volume to 1 litres, i.e. approximately twofold concentration. Dissolved organic carbon (DOC) analysis was then performed using the method of Bartlett and Ross (1998) – as described in chapters 2 and 3. The oven drying process brought DOC concentration to 65 mg C/l from an original concentration of 32 mg C/l. Both concentrated and un-concentrated solution DOC were used in soil batch experiments, while an average solution (48.13 mg C/l solution) was used in the column experiments to mimic river bank filtration (RBF) process on river bank soils.

5.2.2 River bank material

Aquifer material was obtained from Maiden Castle field on the bank of the river Wear, Durham (54.769°N 1.561°W). The sample site was an eroding river bank which exposed fresh alluvial material (Figure 1) and samples were taken approximately 150 cm below soil surface.

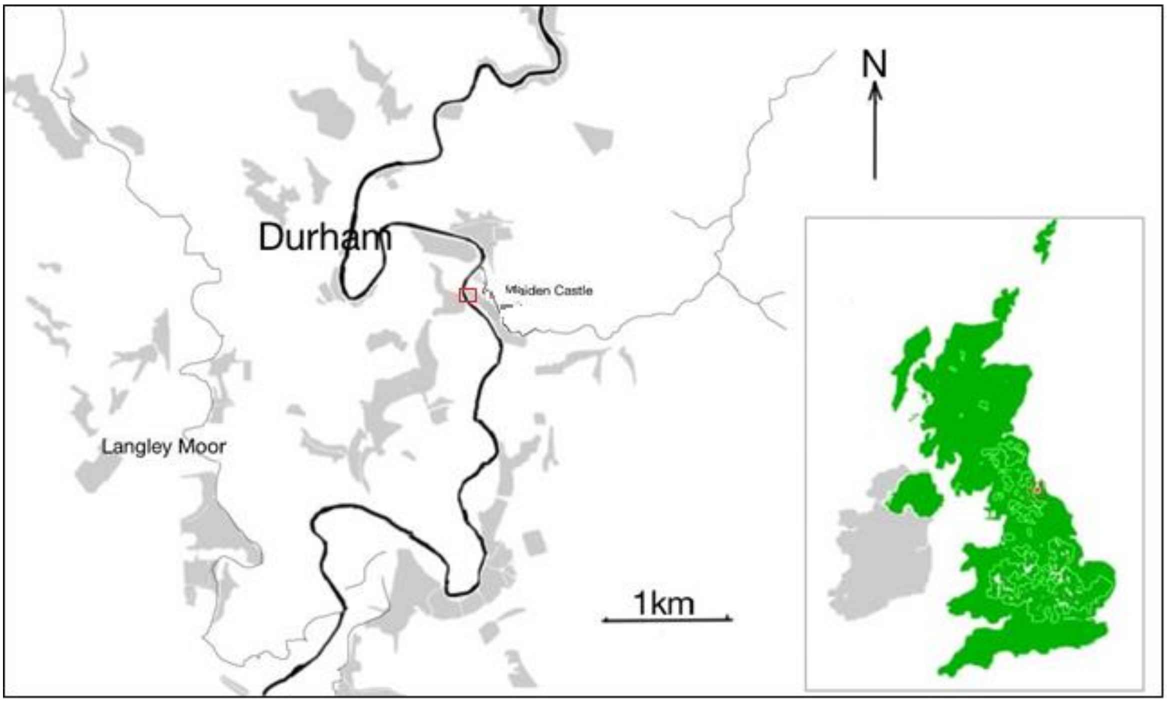

Figure 5.1: Location of Maiden castle (OS grid reference NZ 283 417)

River wear ***Grass land***

The soil above the collected alluvial material is classified as lithomorphic (Avery et al.,1980), which is a clay formed, organo-mineral rich soil. Sub-samples of this aquifer sediment were used to measure the dry bulk density and total porosity (n_t) of the soil using the method described by Boetler (1976). Closed order-end porosity (n_c) was estimated by subtracting the active porosity from the total porosity.

5.2.3 Batch experiments

Solute retardation may arise from adsorption, biological uptake, chemical factions, and matrix diffusion (Hoag and Price, 1997). Adsorption of the DOC on soil is a rapid reaction and the degradation of DOC is a minor factor compared to adsorption in the process of migration in soil (Li and Shuman, 1997). The retardation assumed the linear adsorption isotherm in soil; therefore a batch experiment can be used to predict the retardation in the soil column. The adsorption isotherm for DOC has been found to be linear for soils (Jardine et al., 1989; Li and Shuman, 1997). Although later studies (Baumgarten et al., 2011) found the soil adsorption may not be linear, sandy soil adsorption may be more linear than clayey.

To obtain DOC adsorption information from the river bank samples, a series of batch experiment evaluated at different soil to solution ratios was designed to illustrate DOC changes. Two approaches were included in these batch experiments. A set of eluent dilution experiment was designed to access the changes of DOC adsorption for various solute weights (the river bank samples). The method used in this chapter to get DOC concentration is sensitive to its upper detection limit (around 65 mg C/l). If the eluent DOC concentration is over or close to the detection limit of the method used here, dilution of the eluent would be required to ensure the accurate DOC concentration. Besides the effects to access the type one error of the DOC methods, the eluent dilution batch experiment was also designed to use the distilled water (DI water) as the original eluent to access the DOC released from various soil to solution ratios (river bank samples).

5.2.3.1 Eluent dilution experiment

Three sets of 5 polyethylene bottles (120 ml volume) were used in this study, each set of them were numbered from 1 to 5. The experiments were conducted with varying masses of river bank sample (60g, 50g, 40g, 30g, 20g respectively), which were mixed with the standard DOC concentration solutions (32 mg C/l) in the first set of bottles. Therefore, 5 soil to solution ratios (1:2, 1:2.4, 1:3, 1:4 and 1:6 w/v) were used in the eluent dilution experiment. The original eluent water were then diluted twice and added to two polyethylene bottles. Additionally, a pair of batch experiment was conducted using DI water as eluent. The 25 bottles of suspensions were shaken for 48 h in the dark at 20 ^{o}C. The suspensions were then centrifuged at 3000 min^{-1} for 15 minutes. Supernatants were then filtered through 0.45 µm filters. The solutions were then analysed for pH and conductivity. Eluant DOC concentration was measured using the method of Bartlett and Ross (1998). Relative DOC concentration changes were calculated as $C/C_{o.}$ where C represents the solution DOC concentration and C_o is the original DOC concentration from the standard solutions.

Sorption of DOC to the sampled soil was analyzed by use of the initial mass (IM) relationship (Nodvin et al., 1986). The initial mass method has been a common way to access DOC sorption in soils (e.g. Kaiser et al., 1996; Kothawala et al., 2008). The IM approach plotted the concentration of DOC adsorbed or released (Normalised to soil mass, mg/kg, RE) against the initial DOC concentration of the eluent (Normalised to soil mass, mg/kg, X_i). The regression given below:

$$RE = mX_i - b \qquad \text{Eq 5.1}$$

The gradient of linear regression (m) is a partition coefficient which measures for the affinity of the DOC to the eluent. The intercept b is named as desorption term which indicates the amount of DOC released from the soil when the eluent DOC concentration is zero.

5.2.3.2 Soil wash experiment

Batch experiments of eluate dilution were evaluated at 10 different soil to solution ratios (1:12, 3:40, 1:15, 7:120, 1:20, 1:24,1:30, 1:40, 1:60 and 1:120 w/v). The ratios were defined by the variances of the soil weight applied to the solution range from 10 g to 1 g, respectively. Soil weight changes were minimized in each individual experiment bottle between each wash. The batch experiment used DI water as eluent. Suspensions were then centrifuged at 3000 min^{-1} for 15 minutes. Supernatants were then separated from the soil. Same analysis of the eluent dilution was applied on the supernatants. A wash was performed by adding DI water to each individual bottle to bring it up to its original solution volume (120 ml). Analysis of DOC was applied on the wash supernatant. The wash of the soil was repeated three times.

5.2.4 Column Experiment

A 0.60 m long soil core was taken from a Durham river bank. The core was transported to the laboratory and repacked in the column of the height of 65 cm and diameter of 15 cm (Figure 2). At the 15 cm tall position of the column, a 15 mm dimension hole was drilled. A collecting pipe was installed in the middle of the column and linked with a 1 meter long tube (15 mm diameter). The tube was then linked to a peristaltic pump set to work at a rate of 0.2×10^{-3} m/s, there are 34 cm soil packed in between the collecting pipe and the bottom of the elution water. Underneath the collecting pipe, 15 cm sandy soils were packed up to the bottom of the pipe.

The experimental setup consisted of one unsaturated column of repacked river bank sediment within a cylinder of inner diameter 150 mm and length 1m - the setup is shown in Figure 2. The column experiment was conducted at room temperature (approx. 22^{o}C). Influent water (previously kept at 4^{o}C in the fridge) was brought up to column temperature before application to the columns by placing a portion of the influent tubing in a warm water bath.

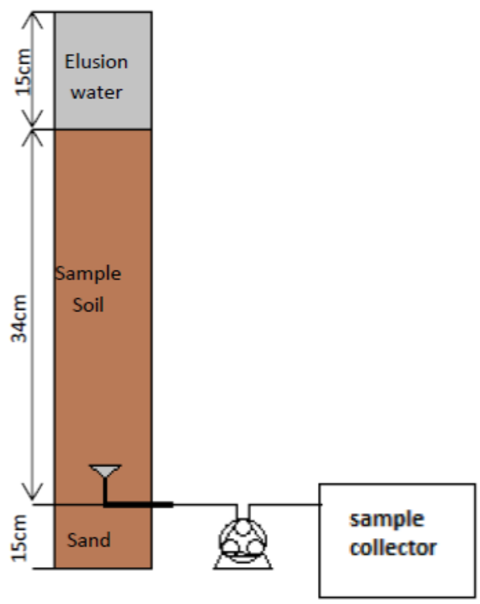

Figure 5.2: Experimental column set up.

Four small holes were drilled at 1 cm below the top of the column. By doing so, a 15 cm deep water table was maintained during every refilling of eluting water. The refilling rates were kept constant during each run, albeit rates varied between runs. Three refilling times were selected, 75 min, 90 min and 180 min. Three refilling times were then referred to as

RF1, RF2 and RF3, respectively, in later analysis. The DOC sorption curve was measured by plotting DOC changes vs time on each individual run. In this experiment, DOC flux changes between the extracted solution and elution water were the same as the DOC concentration changes because the pumping rates were constant during each experiment. Source eluent water DOC concentration remained constant during all tests (48.13 mg C/l). Following each run, the column was flushed with distilled water for 3 hours and drained to ensure similar starting conditions between each run. Similar to the batch experiment, this column study used both distilled water (DI) water and DOC water as the eluent. DI water was applied to the column to access the control data while the DOC eluents were used as the experimental eluent. Experiments started with three days of the distilled water (DI) run through the column. The average elution time was measured as the time from the introduction of the sample at the top of the column to the first appearance of DOC in the collected waters. DI water was used to perform three blank runs with refilling time of 75 mins, 90 mins and 180 min which were named as event RF1, RF2 and RF3. In the first three days of the RF1 experiment, elution water was added by different time gaps. 200 ml eluent was adding in the system to top up the column. The first day of RF1 experiment the run was for 120 mins. No additional elution water was added to the system except at beginning of the first day of the RF1 experiment. The elution water extracted from three blank runs were collected as the control data. Following the three blank runs, DOC eluent water was applied to the column system. The collected samples were immediately filtered upon collection through a 0.45 µm filter and then pH, conductivity and DOC concentration were measured. In the experiment, the eluate DOC concentration over eluent DOC concentration was used to indicate the concentration changes over each individual run. In addition to DOC changes, experimental eluate DOC concentration relative to control eluate DOC concentration

(Relative DOC) under three different refilling times was used as indication of changes in the river bank sample adsorption/desorption.

5.3. Results and discussion

5.3.1 Results of the batch experiments

5.3.1.1 Results of eluent dilution experiment

The bulk density of the infilling river bank samples used in experiment was 1.23 g/cm^3. The C/C_o increased with the decreasing elusion water DOC concentrations in the batch experiment. The DOC concentration changes between different soil weights are small in the lower elution water concentrations with an average 6.43% DOC concentration changes after the first dilution and 6.98% after the second dilution. DOC concentration changes between different soil weights were bigger in the original elusion water, which merely reached 8.52% concentration changes (Table 5.1). Overall, the batch experiment with elution water didn't find significant DOC concentration changes between soil weights in the range used. Results of batch experiment on DOC solute transport also didn't show any clear link between the different pore volumes used (Table 5.2).

	DOC original	Average C/C_O	Changes between different soil weights
Original	33.23	1.66	8.52%
1st Dilution	16.62	3.63	6.43%
2nd Dilution	8.31	7.54	6.98%

Table 5.1: DOC changes over original DOC eluent concentration after two dilutions.

	DOC (mg C/l)	Soil Weight	Pore Volume	C/C_o
	66.51	60.00	0.33	2.00
	53.44	50.00	0.28	1.61
Original DOC	48.05	40.00	0.22	1.45
	52.15	30.00	0.17	1.57
	55.49	20.00	0.11	1.67
	64.21	60.00	0.33	3.86
	66.00	50.00	0.28	3.97
1st Dilution	57.79	40.00	0.22	3.48
	55.23	30.00	0.17	3.32
	58.05	20.00	0.11	3.49
	65.49	60.00	0.33	7.88
	55.49	50.00	0.28	6.68
2nd Dilution	67.03	40.00	0.22	8.07
	58.82	30.00	0.17	7.08
	66.26	20.00	0.11	7.98

Table 5.2: results of batch experiment of DOC concentration and C/C0 ratio under different soil weights applied in each dilution experiment process.

In all 6 soil to solution ratios, the sorption was described by the IM isotherm. Linear regressions use eluent DOC concentration (mg DOC per kg soil) against sorbed DOC concentration in different soil to solution ratios. The coefficients of determination (r^2) for the sorption of total DOC ranged from 0.85 to 0.95 (Table 5.3).

soil to solution (w/v)	Equations	r^2	p
1:2	$RE = 0.9989X_i - 63.885$	0.90	<0.0001
1:2.4	$RE = 1.1455X_I - 59.846$	0.85	<0.0001
1:3	$RE = 1.4828X_I - 66.256$	0.92	<0.0001
1:4	$RE = 1.1675X_i - 61.897$	0.92	<0.0001
1:6	$RE = 1.2657X_i - 67.218$	0.95	<0.0001

Table 5.3: Comparison of the soil to solution ratios and amount of DOC released from soil.

In Table 5.3, parameter b (intercepts of equation) represents the DOC released from the soil when the eluent DOC concentration is 0 mg/kg. Comparing the different soil to solution ratio on the parameter b, the ratios differences influence on b was found to be minor. A regression including all soil to solution ratios were listed below:

$$RE = 1.21\ X_i - 63.8 \qquad \text{Eq 5.2}$$

The r^2 of equation 1.2 is 0.85 and P value is smaller than 0.001. The parameter m (1.21), was dependent from the changes of ratios. The IM isotherm indicates an average of the 63.8 mg/kg DOC will be released from sample soil in experiments.

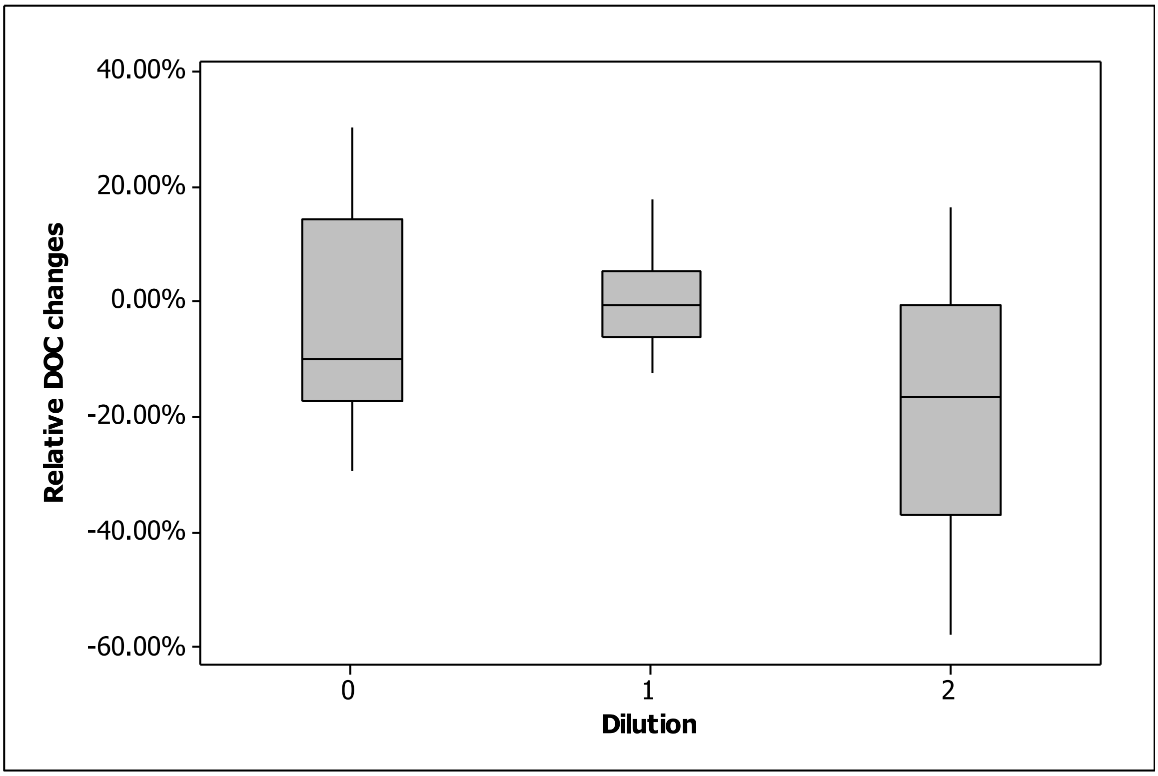

Figure 5.3: Boxplot of the relative DOC changes over 2 dilutions in eluent dilution experiment.

. Results (Figure 5.3) showed relative DOC concentration changes were decreased over all three eluent DOC concentrations. The original eluent DOC concentration batch had a median relative DOC concentration of -9.8%. First dilution and second dilution had the relative median DOC changes of -0.5% and -16.5%, respectively. The negative relative DOC changes indicated the adsorption of the river bank samples after the batch experiment. In Figure 5.3, the relative DOC changes weren't increased or decreased with dilution of the eluent, although both Table 1 and 2 indicated that the DOC changes were increased in all batch samples. The adsorption may therefore need longer travel distance to build up the better removed rate and eventually suppress the eluent DOC concentration. Figure 5.4 showed relative DOC changes over different samples weights. In all 5 median values of the relative DOC changes over soil to solution ratio, only the 1:4 ratio (30 g soil) has a positive reading of 1.2%. The rest of the sample weight had the relative DOC changes of -13.4% (1:6), -5.3% (1:3), -0.5% (1:2.4), -11.5% (1:2). The positive reading of relative DOC concentration indicated net desorption of DOC and the negative reading indicated the adsorption of the samples. Majority of the samples in this eluent dilution experiment showed adsorption of DOC. However, the relationship between soil to solution ratio and relative DOC change was not linear. Exceptions of the soil to solution ratios and relative DOC changes may be due to the turbulence of the shaking table overnight i.e. clogging may formed prior to the shaking on some samples therefore limited the sample interaction with the eluent.

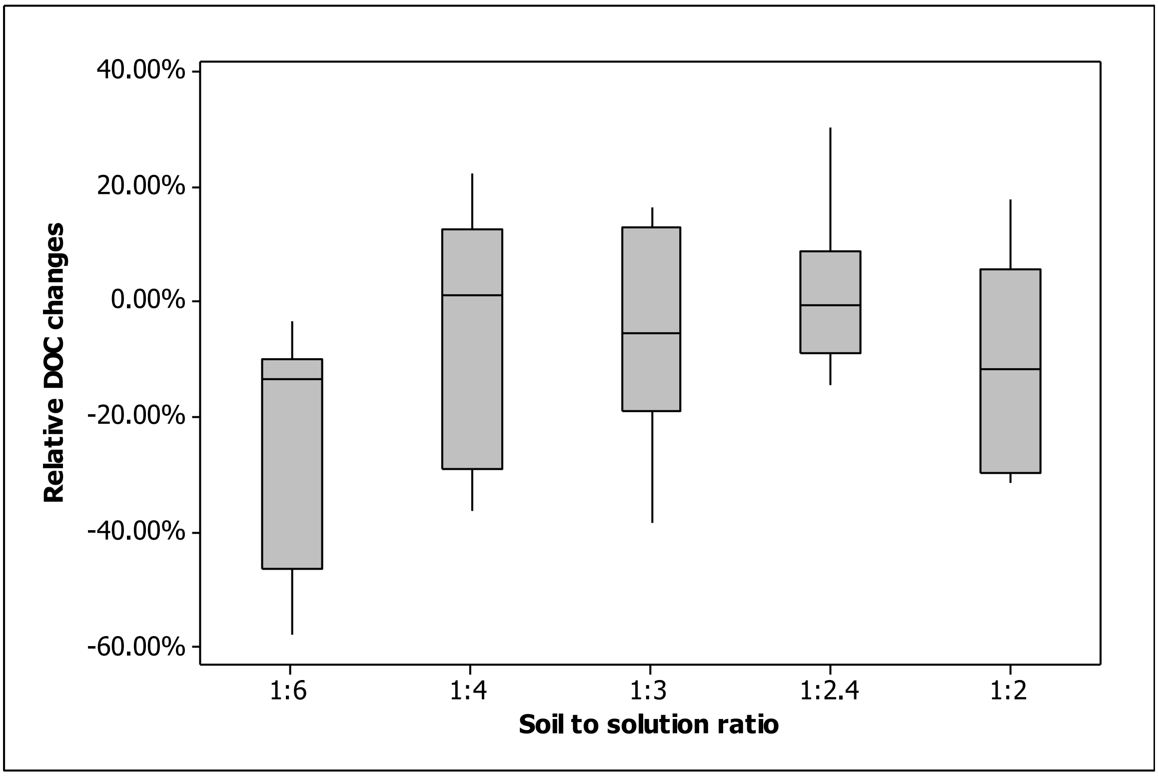

Figure 5.4: Relative DOC changes over different soil to solution ratios.

Comparison of the IM isotherm and relative DOC concentration over dilutions found that soil adsorption of DOC were the dominated Figure of sample soil sorption albeit the much smaller initial eluent DOC (33.2 mg/kg) input compare potential DOC desorption b (63.8 mg/kg).

5.3.1.2 Results of soil wash experiments

The solute was then changed from stream water to the DI water. In total 10 different soil to solution ratios were chosen to evaluate the DOC sorption to soil. Despite different soil to solution ratios applied in eluate dilution process, DOC concentration maintains on average of 60 mg C/l. In total 20 samples in 2 batches, DOC concentration varied from 52 mg C/l to

62 mg C/l.. After 3 washes, solutions concentrations from 60 samples in 6 batches still showed an average DOC concentration of 59 mg C/l ranging from 48 mg C/l to 63 mg C/l.

Results of batch experiments showed large export of DOC in both elusion water and DI water. Desorption from the soil may be the source of the continually high DOC concentration in the solution. In between each wash of distilled water conductivities were significantly decreased from 91 to 20 S/cm albeit solution pH varies between 5 and 6. The changes of pH and conductivities may be caused by the changes of DOC concentration.

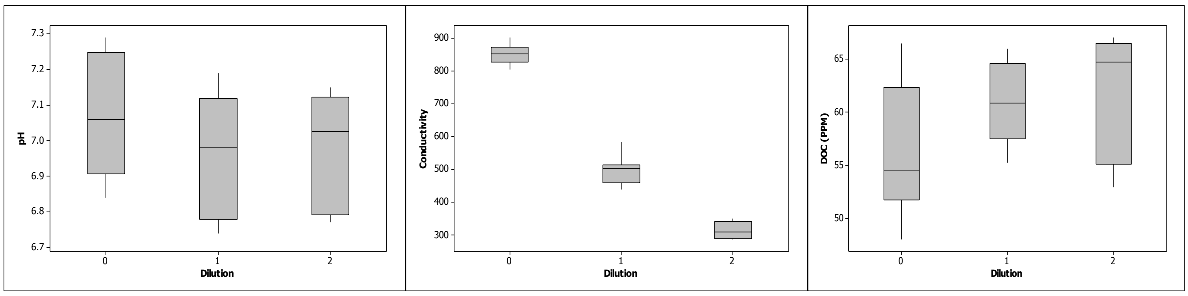

Figure 5.5: DOC concentration changes / solution hydrological changes over eluent dilute process.

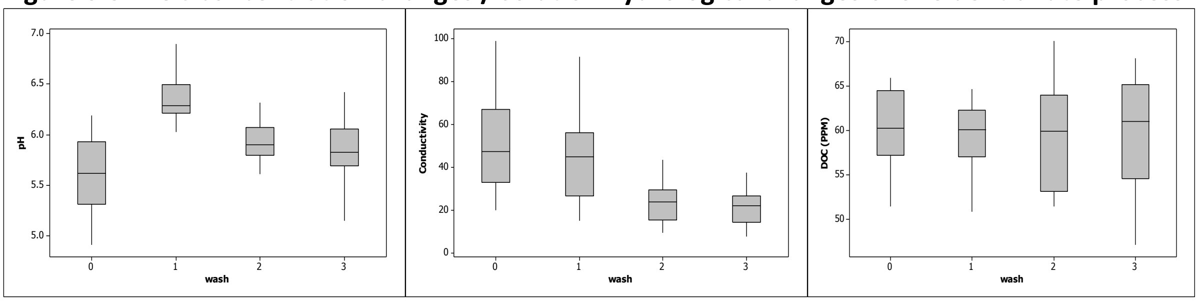

Figure 5.6: DOC concentration changes / solution hydrological changes over wash process.
Where 3 graphs stand for pH, conductivity and DOC changes between each dilution and wash process, respectively.

Figure 5.5 shows the comparison between eluent dilution processes that were applied in the soil batch experiments. Results of these dilutions process showed that both pH and conductivity of the solution decreased with increased number of dilution steps. The DOC concentration from the solution increased with the deceased eluent DOC concentration. The volume of eluent water added to each experimental bottle was the same for the previous dilution process in section 5.3.1.1. As the eluent DOC decreased over each dilution, the increased solution DOC must be sourced from desorption from the soil.

In comparison to the dilution experiment, the soil batch experiment was also designed to use DI water to perform a set of wash experiments. Wash experiments showed a rapid increase of pH between the original solution and the first wash (9.6%). From first to third washes, solution pH decreased. The conductivities decreased with increased washing times. Median of DOC concentrations remained the same between each wash. Similar to the earlier dilution process, the volume of DI water added to each bottle remained the same between each wash (Figure 5.6). Although the b from IM isotherm varies with the different soil to solution ratios, the DOC concentration between each wash in Figure 5.6 appeared to be relatively stable. The stable DOC concentrations after each wash indicated equilibrium may have existed during the experiment.

5.3.2 Results of the column study

5.3.2.1 DI eluent experiment

The first set of column studies on the DOC concentration changes during the first three days of experiment were performed using distilled water as the eluting solution (Figure 5.7). Although all three experiments were conducted using different experimental duration, only the first day of experiment showed a potential breakthrough curve over the 60 minutes of the experiment. The oscillation of DOC concentration between 10 mg c/l to 50 mg c/l is observed between RF2 and RF3.

During the RF1 (75 min) experiment (Figure 5.7), DOC concentration changed from 38.8 mg C/l to 57.9 mg C/l in first 15 min of the experiment. DOC concentration then slowly decreased from 57.9 mg C/l to 48.3 mg C/l during the next 45 mins before a small increase on the end of first day experiment (49 mg C/l). Unlike the smooth transition of the DOC concentration changes in the first day, the two experiment lengths RF2 and RF3 illustrated DOC concentration from extracted solutions from column had rather constant changes in times of 15min or 30 min.

Figure 5.8 shows the whisker plot of DOC concentration changes over three running times. Three median values were observed 52.32 mg C/l for RF1, 26.97 mg C/l for RF2 mins and 35.12 mg C/l for RF3. With the extension of the running time, DOC concentrations decreased, except RF3 where the median value here were slightly increased to 35.12 mg C/l compared to 26.97 mg C/l in the 90 mins run.

In general, ranges of DOC concentration for the last two days of the experiments fluctuated on average by 40 mg C/l compared to changes on the first day experiment where DOC concentrations only changed on average by 15 mg C/l (Figure 5.7). The rapid changes of DOC concentration in solution showed the release of DOC from soil is a rapid desorption - there was about 30 mins in between the concentration peaks.

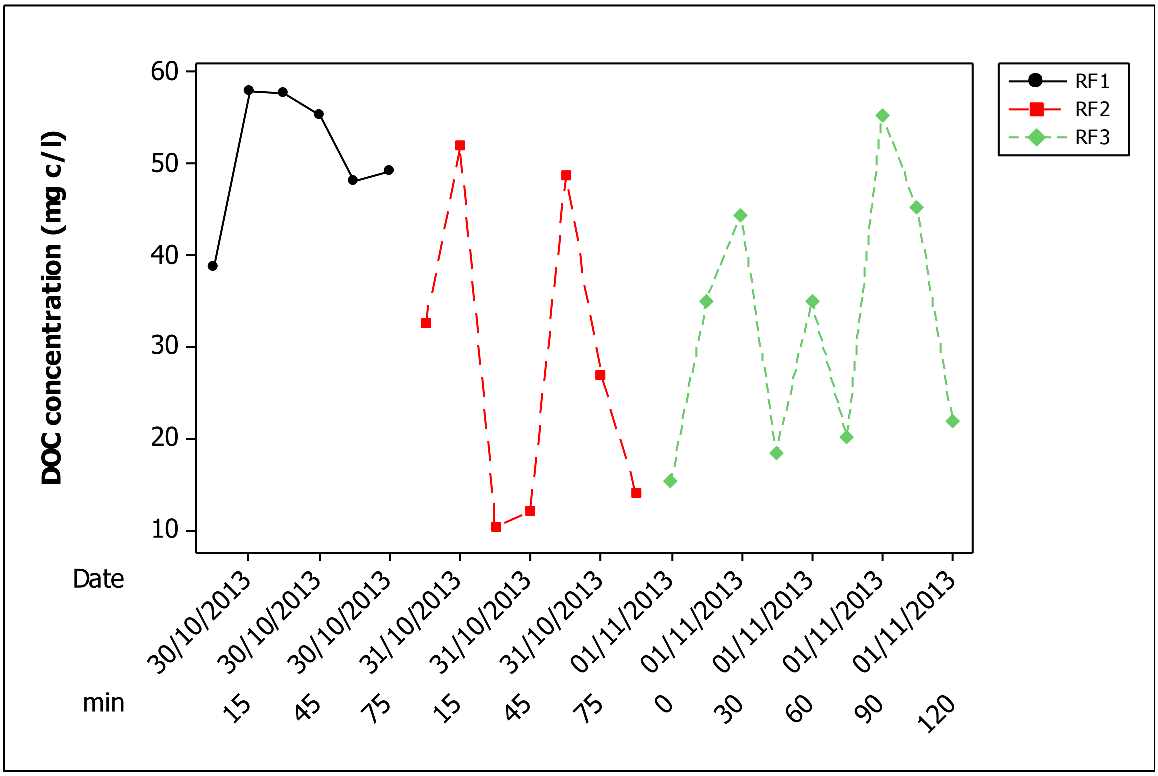

Figure 5.7: DOC changes over three running time RF1 (75 mins), RF2 (90 mins)and RF3 (180 mins) among blank samples.

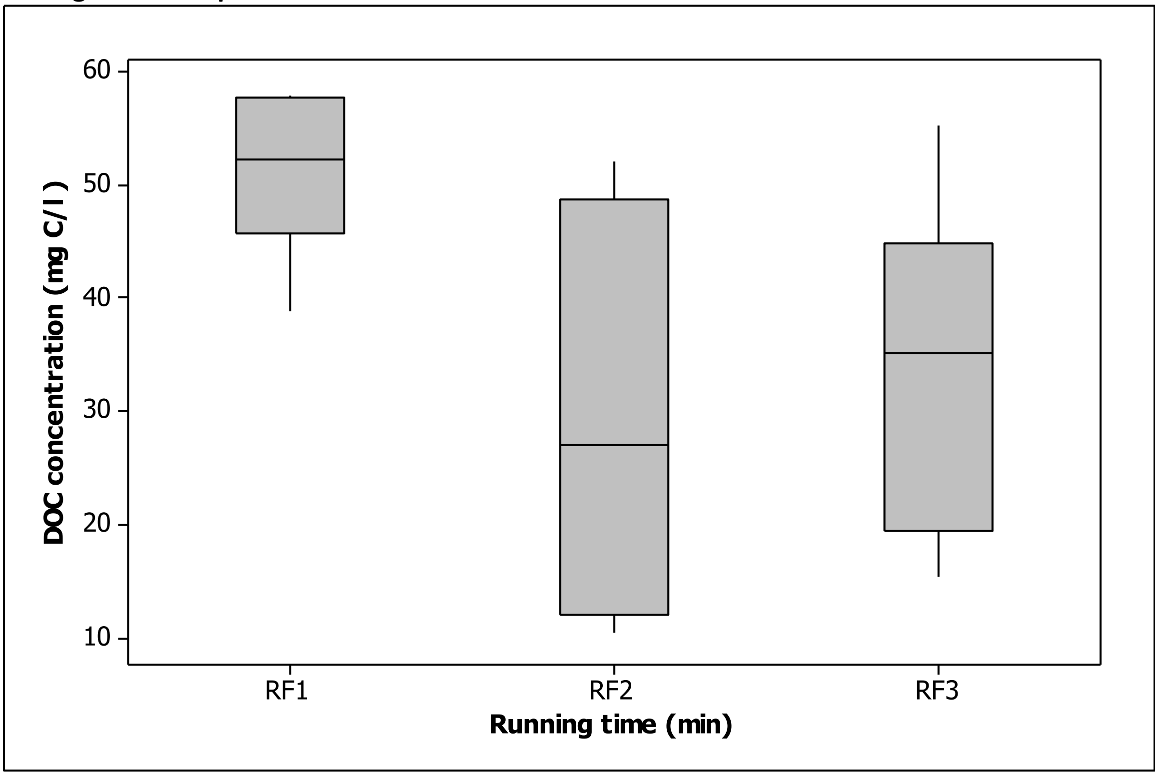

Figure 5.8: Eluate DOC concentrations under DI eluent with different running time. The upper whiskers (top 25% of data) of RF1 are too close to up boundary of interquartile box to shown in figure.

5.3.2.2 DOC eluent experiment

5.3.2.2.1. 75 mins (RF1) experiment

The results of soil column studies were then conducted using a 48.13 mg C/l concentration DOC eluent. From 04/11/2013 to 06 /11 /2013, DOC concentration changes were monitored in comparison with the original DOC concentration of eluent used in the experiment. Results of the first day experiment showed a rapid decrease of DOC concentration and flux changes (Figure 5.9). The flush of elution water brought about the positive increase in DOC compared to the original DOC concentration changes in the first 30 mins; DOC concentration reached the lowest point after 75 mins. Immediate after 75 mins, DOC concentration returned back to a relative high DOC concentration in the next 15 mins. Similar changes of DOC concentration were observed in the next two days of the experiment. Differences of the experimental design of the time between each eluent top up may cause the different lag time of the appearance of DOC concentration peaks in each day.

Figure 5.10 shows the eluate DOC changes from DOC eluent relative to eluate DOC from DI eluent for the RF1 experiment. Relative DOC concentration has the median values of – 63.7% among non- refilling samples and median values of -67.9% in refilling points. The negative value of the relative DOC changes indicates the adsorption of river bank samples were the main driver of the DOC changes through the RF1 experiment.

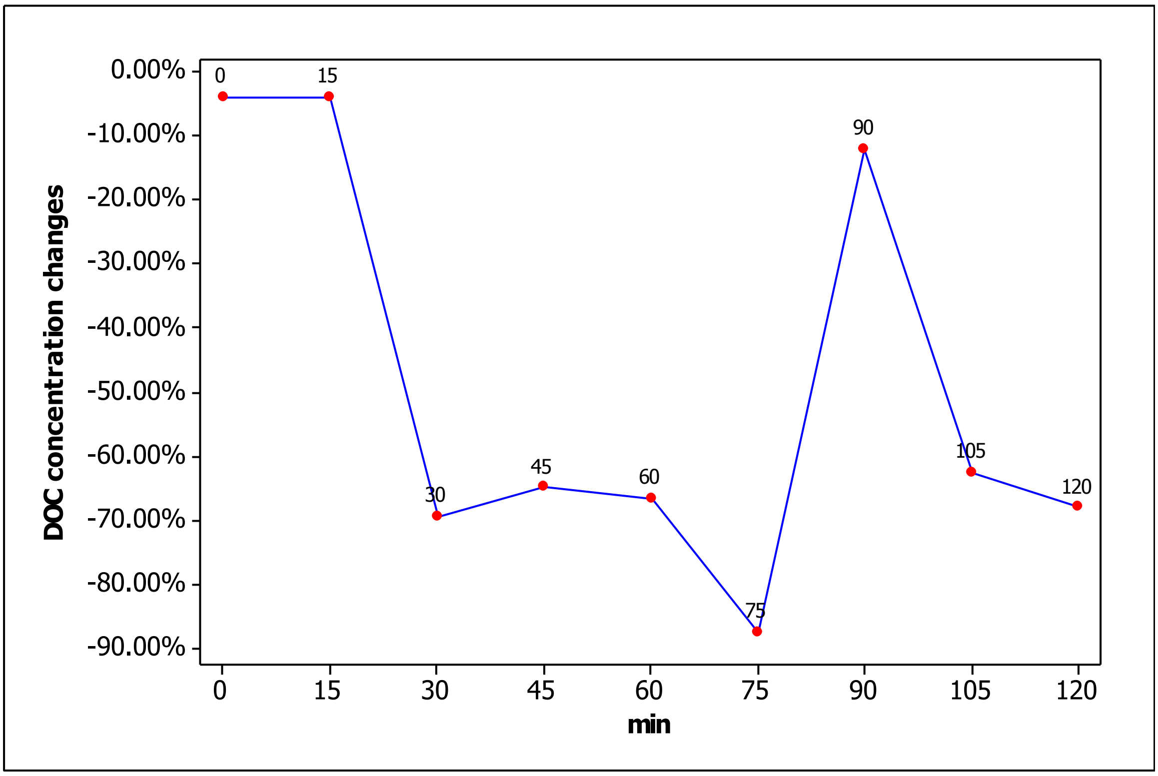

Figure 5.9: time series of DOC changes on every RF1 experiment.

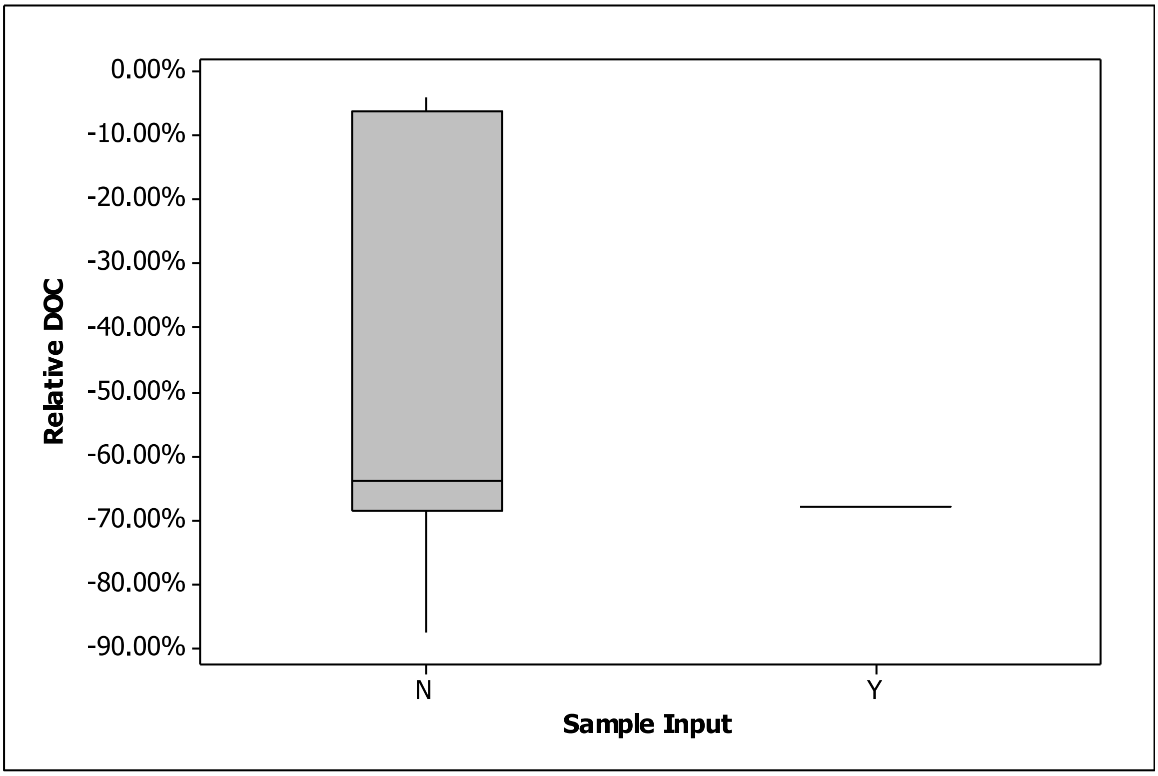

Figure 5.10: Relative DOC over RF1 experiment. There was only 1 time sample input, therefore the plot box of Y is represented as a single line.

5.3.2.2.2. 90 mins (RF2) experiments

200ml of DI water were added to the system every 90 mins. Results after 300 mins of experiment showed three concentration peaks relative to the original elution water concentration. The water refilling points are on average 15 – 30 mins before the concentration changes. All three peaks represented positive concentration change relative to the original DOC concentration in the elution water. From the earlier studies, the solution took 22 mins on average to run through the column (Figure 5.11).

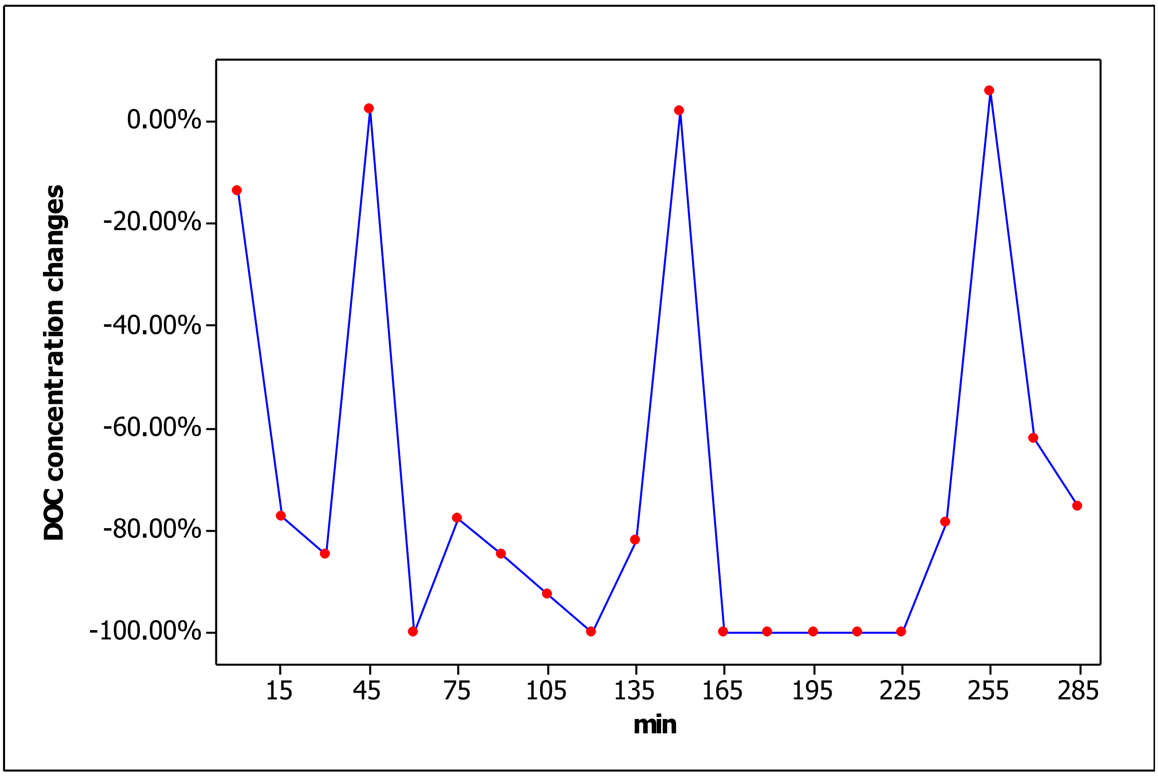

Figure 5.11: time series of DOC changes on first day of RF2 experiment.

Like the RF1 experiments, the 90 min experiment was extended to a second day. Results showed appearances of positive peaks in the time series of DOC concentration (Figure 5.12). The time gap between each refilling was 90 min. During the 570 minutes of the experiment, there were 6 concentration peaks observed. There are 5 data point maintained in the same concentration changes after the second peak. The absorbance of 5 samples is over the limit (60 mg C/l) of the top measurement which means their actual DOC concentrations were too small to measure.

During the 2 days of the experiment, DOC concentrations decreased by 75% compared to the DOC concentration in the elution water. The peak concentrations increased 3.4% compared to the original DOC concentration. The DOC concentrations increases may be due to soil to solution equilibrium illustrated by batch experiment changes.

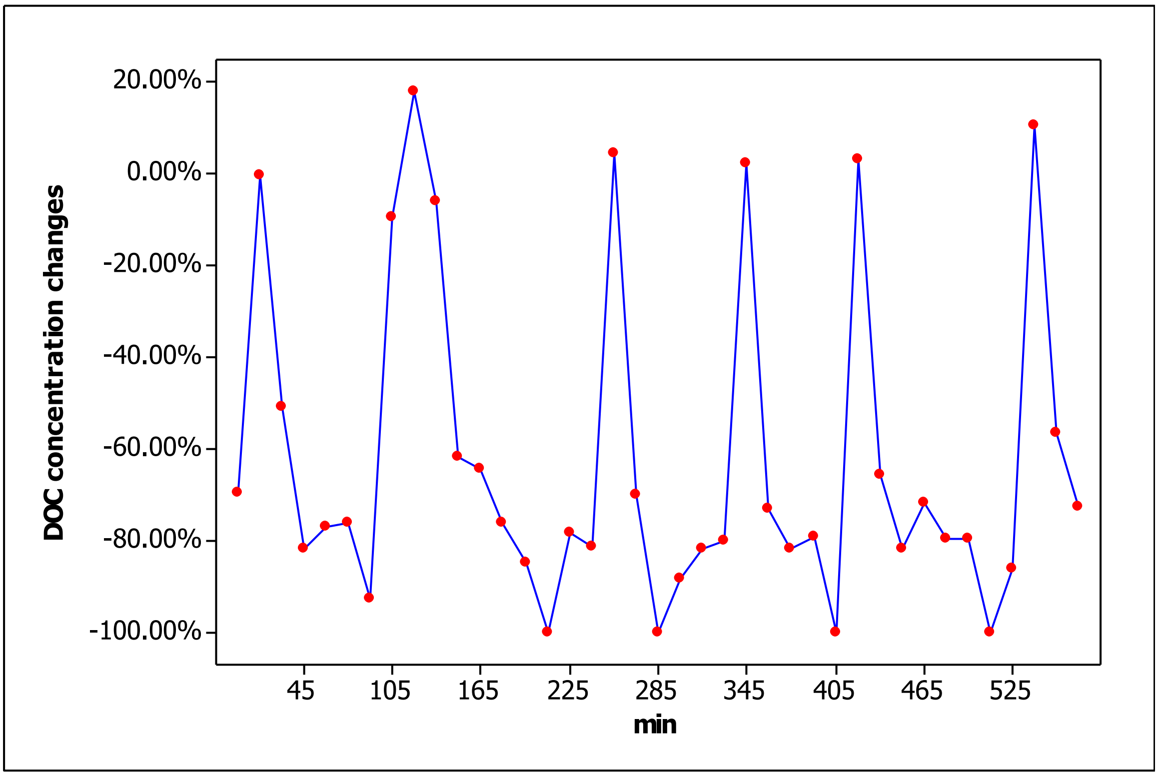

Figure 5.12: time series of DOC changes on second day of RF2 experiment.

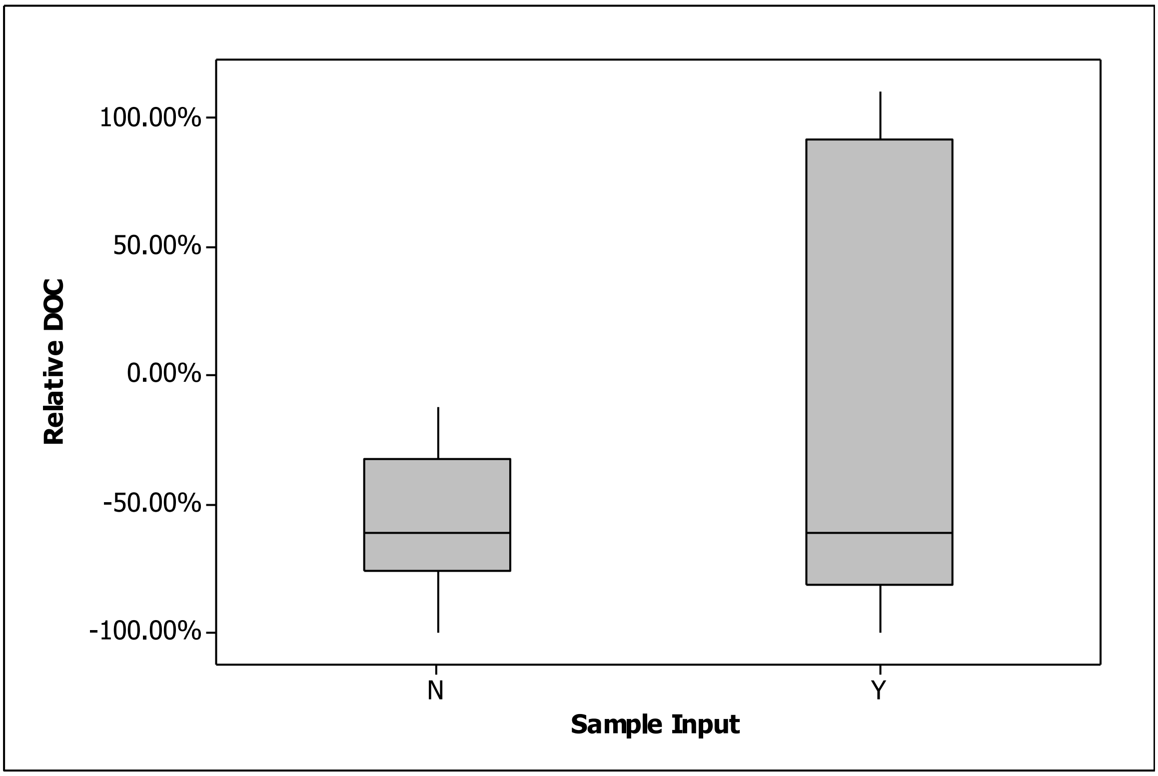

Figure 5.13: Relative DOC changes during RF2 experiment.

Figure 5.13 shows that relative DOC changes over the 2 days of 90 mins experiment. The median relative DOC changes on both refilling samples and non-refilling samples were -61.2% and 61.6%, respectively. Similar to the earlier 75 mins experiment, adsorption of the river bank samples were the dominant factor during the experiment. The peak in the DOC changes per se is the therefore merely the reflection of the refilling.

5.3.2.2.3. 180 mins (RF3) experiments

The time gap between each refilling was extended to 180 mins on the RF3 experiments. The results RF3 experiments showed the time gap between two peak concentrations extended to 90 mins and DOC concentration increased to a maximum of 35% greater than the original elution water concentration. The RF3 experiment was conducted three days after the previous RF2 experiment. During the three day experiment gap, the water table went down about 2 cm. No additional water was added during the time between the two experiments. The first day of the RF3 experiment had two concentration peaks (Figure 5.14); both of them appeared 30 mins after the refilling of the sample water. Two DOC concentration peaks represented increases in DOC concentration relative to the eluent DOC concentration. The majority of samples collected reflect decreases in the DOC concentrations after water has run through the column. Figure 5.15 shows median value of the relative DOC changes in no-refilling samples of -58.5%. Median values of refilling samples increased 1% compared to the no refilling samples.

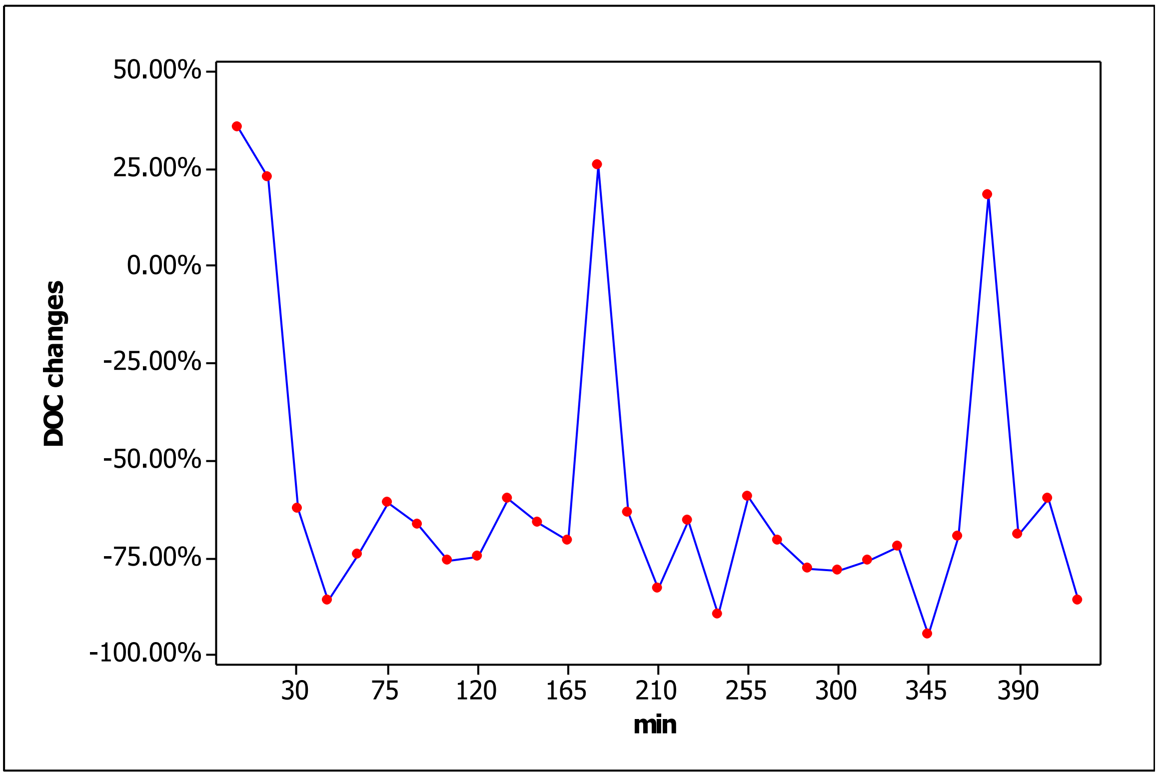

Figure 5.14: time series of DOC changes on every 180 mins refiling

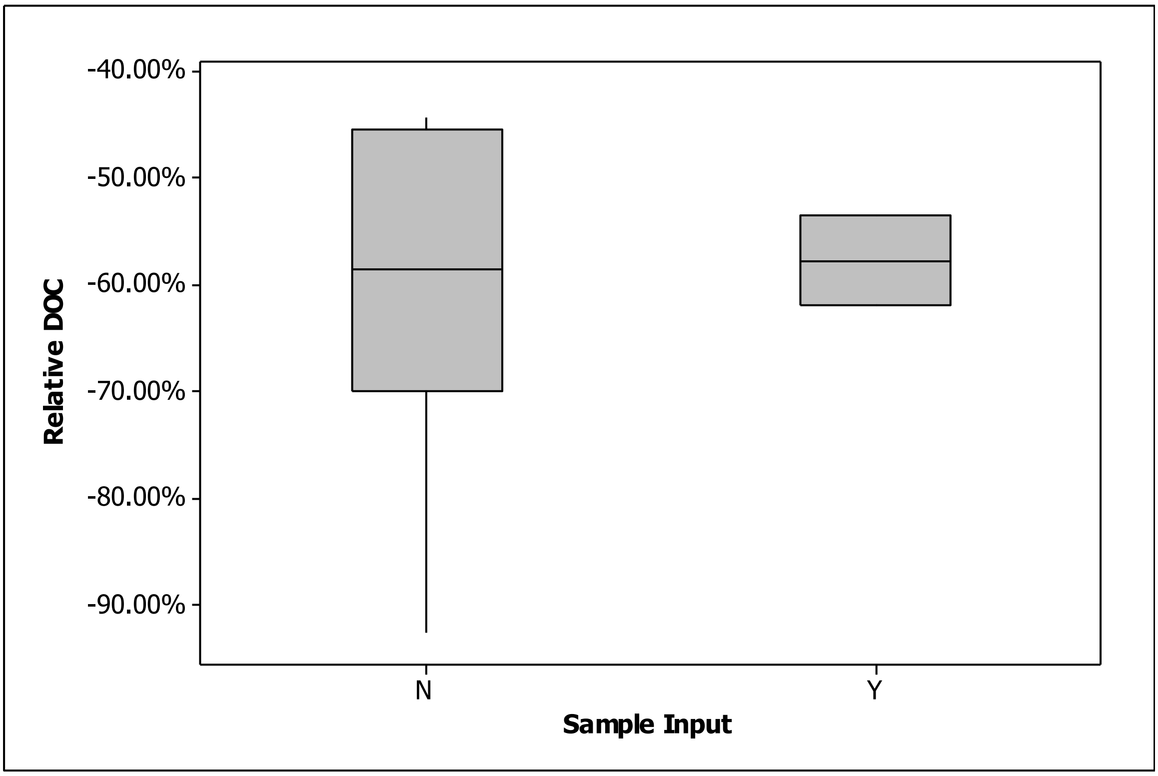

Figure 5.15: Relative DOC changes during 180 mins experiment. During the experiment, there were only two times sample inputs, therefore the upper and lower boundaries of Y were same as interquartile box.

When the experimental time was extended to 720 min, similar DOC concentration trends to the RF2 experiment were observed (Figure 5.16). The time between each refilling was on average 90 mins. The exception was between the third and fourth refilling, which has a time gap between each refilling of 180 min. The peak of the concentration peaks appeared 15 to 30 min after each refilling. The majority of the DOC concentrations showed a reduction compared to the original elution water concentration. Between peak 3 and peak 5, refilling time were increased to the 180 min, the DOC peak shifted with the increased time between elution.

During the experiment, DOC peaks were observed between 15 mins to 30 mins after refiling eluent to the system and stayed relatively stable compared to the negative changes observed from DOC concentration. It is most likely the DOC peak was brought up by the refilling of the elution water. During 720 min, the delay of the DOC concentration peak increased with the extension of the time between each refilling. Average peak DOC concentration increased from 3.4% to 20% as the extension of refilling time increased. All three experiments (RF1 , RF2 and RF3) observed an increase of pH over the experimental time, albeit conductivity of infiltration samples showed no clear relationship within the experimental time series. The relatively stable DOC peaks seem strongly associated with refilling of the water, which indicates these peaks were the delayed appearance of refilling the elution water.

During all three experiments, the eluent water was maintained at the same DOC concentration. The majority of the DOC was removed through running through the column, with average reduction in DOC concentration being 74%. Even with the extended time between each refilling, the removal of DOC still didn’t achieve any form of breakthrough curve or equilibrium of DOC removal. Relative DOC changes in between three experiments (Figure 5.17) were slightly increased with the increasing refilling time gap. The extension of the refilling gap leads to longer running time, therefore the longer running time seemed to decrease the adsorption (increased desorption) by the river bank sediment. The batch experiment indicates soil sorption is independent to the different soil to solution ratios. Therefore, the greater soil content and the greater soil: water ratio of the column experiments relative to the batch experiments may not have an impact on the soil adsorption equilibrium, but the longer running time of the eluent should enhance the sample removal process.

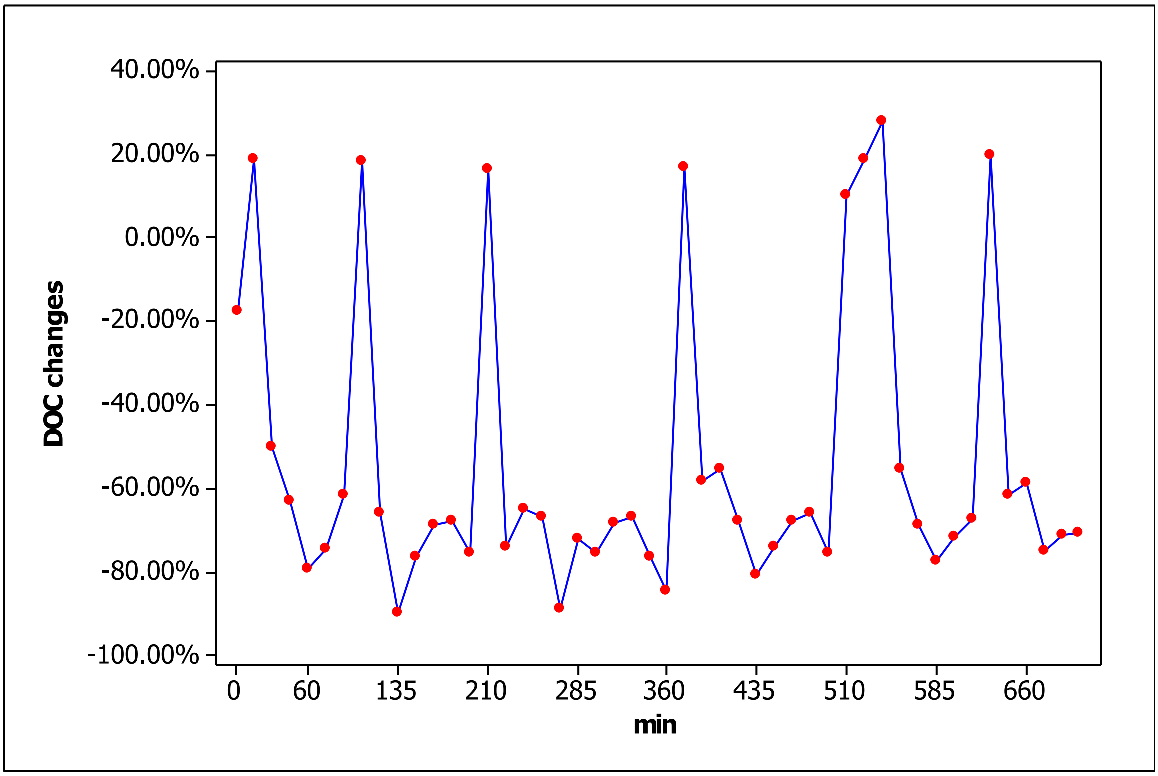

Figure 5.16: time series of DOC changes on extended time

Batch experiments indicated an equilibrium of DOC with the soil. However, the column studies showed adsorption of influent DOC. After two days of blank runs, the system may have converted to anaerobic which would lead to enhanced DOC removal. During the entire column experiment, no clear pH and conductivity changes were observed. The DOC changes are mainly controlled by the soil sorption. The peaks observed in the column study commonly appeared after refilling of the eluent DOC. The observed peaks may be caused by various reasons. One simple explanation is that the eluent DOC passes through micropores present in the soil column. Studies conducted on DOC export in other soil systems, i.e. grassland and agricultural soils, indicate that DOC transport are primarily determined by hydrological regime, especially in the vertical direction (Mertens et al., 2007; De Troyer et al., 2011). Peaks during column experiments may indicate that vertical flux also as a main control of the bank filtration impact. However, the pumping rate used in the column experiment were relatively low compared to the industrial bank filtration, therefore, different pumping rate may overtake the vertical water flux to control the DOC transport through soil. Kaiser and Zech (1997) indicted a relationship between reduced DOC sorption at the greater DOC addition. Here in the column study, the additional DOC by refilling may just indicate the rebalance of the soil solution equilibrium since especially that eluent DOC concentration are much smaller than the potential desorption DOC concentration of sampled soil.

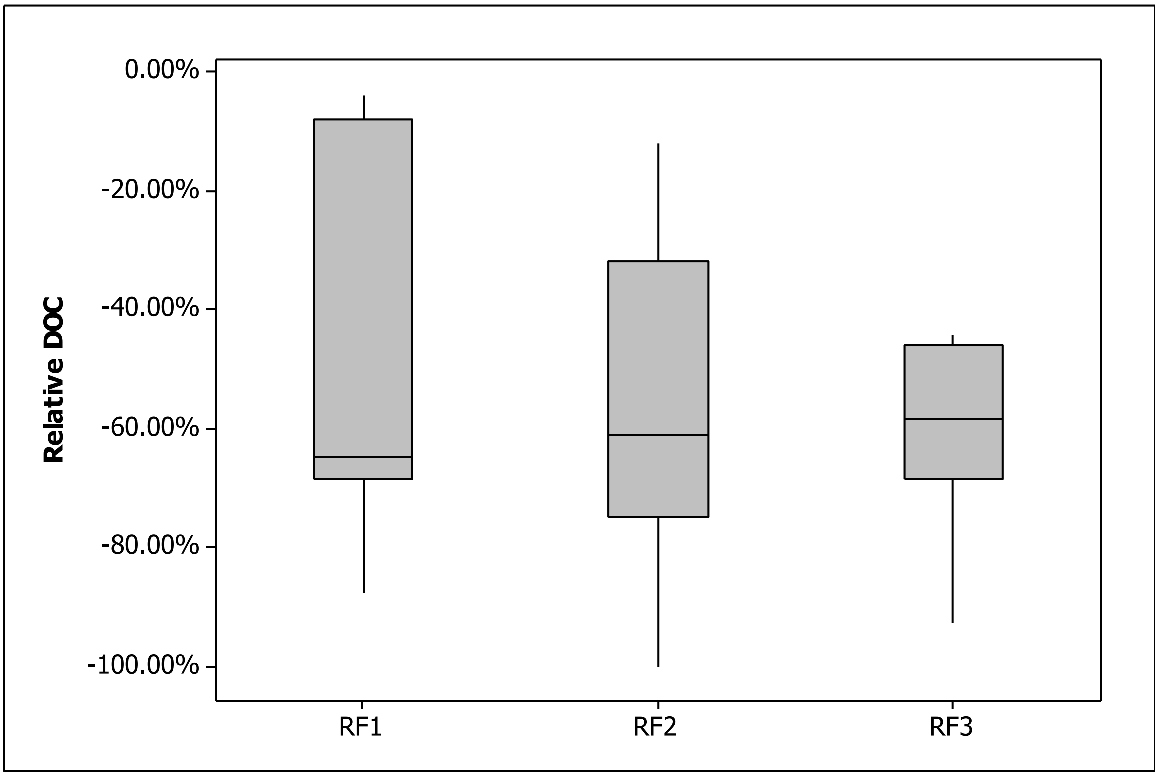

Figure 5.17: Relative DOC changes over three experiments

5.4 Conclusions

In the batch experiment, the isotherm result indicated an average of 63.8 mg C g/l desorption would occur in the soil sample applied in this study. With the elution DOC concentration varying from 8 mg C g/l to 32 mg C g/l which are much less than the initial DOC concentration desorbed from soil. The soil batch experiment still shows the strong feature of DOC absorption. DOC was successfully removed by running through a soil column with the average removal rate of 74% relative to initial concentration. Numerous stable DOC peaks were spotted 15 to 30 mins after each refilling of elusion water suggesting the column may be mainly control by absorption, rather than desorption of the soil. The fluctuations in DOC concentration observed between peaks may be caused by biomass activities or absorption/ desorption equilibrium. No breakthrough curve of DOC concentration was observed in this study.

Chapter 6 Conclusion

6.1 Progress against study objectives

Objective 1

Measurement of the DOC concentration and budget on a series of nested and blocked catchments.

Drainage is a commonly used upland peat management technique in the UK and has driven the interests of researchers as drainage has been associated with increased water colour and changes in carbon storage in peat land. Blocking has been suggested as an alternative to peat land restoration to reduce the water colour and prevent carbon loss. The study, based on four years observation from 2008 to 2012 in Upper Teesdale, Northern England, has shown that both DOC concentration and DOC export did decrease upon drain blocking. For DOC concentration, the effect of drain-blocking was to lower concentration - at larger catchment scales (1 km^2) a 4% reduction was found and a 2.9% reduction for zero order drains. For the DOC export, there was a 7% reduction on first order drains (1 km^2) and 12% reduction on zero order drains. However, it was shown that any observed decrease in DOC export was largely explained by changes in water yield rather than the drain blocking itself. It is possible that the small change in concentration observed at this site is due to the relative small change in water table that was brought about by the drain blocking at this site.

Objective 2

To access the blocking effects upon the peak flow events in upland peat.

A series of analyses were applied to the DOC data gathered from 2008 to 2012. From 4 years of observations a total of 756 peak flow events could be considered. Results of events analysis found that both the change in DOC concentration and the change in DOC flux across an event was smaller after blocking with an average of 4 times smaller in DOC concentration changes after blocking and 55.6 % reduction on DOC flux changes after blocking. Blocking is a significant factor controlling the DOC concentration and DOC flux changes by controlling the event flow in the events analysis. Despite the blocking effects on controlling the event flow, factors such as rainfall total, rain duration, flow lag time, peak flow were also observed as significant factors controlling the event flow. Principal components analysis of the events data indicated interactions between rainfall duration and flow lag time were the more dominant factors controlling the event flow thus the DOC changes of the events.

In general, the effects of drain blocking on DOC concentration changes and DOC flux changes increased with scale of drains after blocking.

Objective 3

To assess bank filtration as an alternative approach to the management of high DOC concentrations.

Bank filtration is primarily used in Germany as an efficient water treatment for bulk contaminants and water colour. The study was aimed to test whether bank filtration could serve as an efficient treatment for DOC removal as an alternative to drain blocking. Instead of conducting a field study, a series of batch experiments and a column study were conducted in the laboratory for 6 months. Soil samples were gathered on the river bank of River Wear, Durham. Results of batch experiments were applied on different soil to solution ratios and showed an average of 63.8 mg/kg DOC will be released from the soil. Despite the initial desorption of DOC from soil been higher than any input eluent DOC concentration applied in the batch experiments, the eluate DOC concentration relative to eluent DOC concentration still showed reduction of relative DOC concentration varying from 0.5% to 16.5%. The batch experiment indicated soil sorption is the key factor controlling the DOC connection changes.

In the column study, the results of relative DOC eluate concentration showed an average of 74% reduction. The DOC concentrations of soil water after the filtration were generally higher than the DOC concentration input. Soil sorption equilibrium was attained between the eluent DOC concentration and soil. The desorption/adsorption status of the soil was shown to responds to the infilling of the DOC eluent. Although the eluate DOC level were higher than the eluent DOC in the column study, the eluate DOC shows the reduction in comparison between the DOC eluent and distilled water eluent. The study indicates that bank filtration could be a useful technique to reduce stream DOC concentration if the stream contains high DOC concentrations. With the soil sample used in this study, an eluent DOC concentration more than 63.5 mg C/l may start to show real reduction in the eluate through filtration. However, the stream DOC concentrations applied in the study were much less than the initial soil desorption DOC concentration observed. Thus, the bank filtration may not be suitable for the studied site. In most of UK highland peat, the stream DOC concentration is also much less than 63.5 mg C/l. Therefore, river bank filtration may an efficient way in controlling the DOC if at an industrial level for heavily polluted water pre-treatment, but seemed not suitable for the normal reservation of DOC management.

Objective 4

to assess the impact of revegetation on DOC changes in upland peat streams.

A year long field study of revegetation effects on DOC concentration and water colour in streams was conducted at Killhope, Northern England. The revegetation effects on DOC concentration and water colour was assessed as relative DOC and relative water colour. In the study, no water sample or the metrological data were taken prior to the start of experiment, therefore, the relative data was not used to assess whether the DOC concentrations or water colour are different between the study catchments but whether the DOC and water colour in the stream runoff in the experimental catchment declines relative to the control catchment with time.

Results of DOC concentration showed the higher DOC concentration in experimental catchments than control catchment with the average of 41.68 mg C/l DOC in experimental catchment and 31.65 mg C/l DOC in the control catchment during the study period. A significant difference in DOC concentration between the sample types was observed. i.e. the difference between catchments is 12.1% higher in runoff samples than in stream water samples. The results for the relative DOC concentration showed no significant trend of relative DOC concentration over the study months. During the study periods, the revegetation was found not to be a significant factor in controlling DOC concentration.

Results of water colour shared some similarities with results for DOC concentration. The experimental catchment had the higher water colour and more humic compounds than the control catchment. The difference of both absorbance at 400 nm absorbance and the E4/E6 ratios are higher in runoff samples in between catchments than in stream water samples. Unlike the relative DOC concentration, the relative water colour observed a seasonal change over the study months. The variation of both relative absorbance at 400 nm absorbance and E4/E6 ratio in between months got smaller from spring to winter. A reverse trend in between relative absorbance at 400 nm absorbance and E4/E6 ratio was also observed which indicates higher water colour but less humic compound were produced between these seasons. Thus, a potential flow path changes may have occurred during the study. In general, the revegetation was found not to be a significant factor controlling the water colour changes. However, the effect of revegetation is much influenced by factors such as rainfall and seasonal changes.

Despite lack of encouraging results of DOC concentration and water colour observed, the effects of revegetation were observed as efficient for maintaining on average 0.16 m higher water table in the experimental catchment than the control catchment and lower variances in evaporation in between months in the experimental catchment (39.2% changes in evaporation between months).

6.2 Study limitations

Limitations inherent in the methods and data used in this study are acknowledged during the study. In the drain blocking and events analysis, the large number of samples collected in the drain sampling campaigns make it impossible 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 both drain blocking and revegetation were conducted. In drain blocking study, six monitoring sites were equipped with a range of scientific instrumentation including automatic water samplers and data loggers set up to monitor flow, conductivity and a range of weather parameters. The extreme weather conditions at the localities leads to the breakdown of equipment at certain times and thus leads to the loss of data. The panels used in revegetation suffered the same severe weather conditions with 1 m deep snow in the bottom of both catchments where the automatic water samplers (along with wiring in the data loggers) got buried from December 2013 to February 2014. The summer of 2013 also had some cruel effects on the sampling at revegetation site, for the 3 months from June to August, both the control and the experimental catchments suffered from extreme dry conditions meaning auto samplers failed (Figure 6.1). Measures were taken to reduce the impact of damage, for example, additional solar panels were installed on both catchments to provide enough power for auto samplers during the winter snow periods. Both auto-samplers were also moved to the higher position to avoid entirely being buried by snow. In the dry summer, the spot samples were taken in addition to the auto samples and traced all the way down to the main stream in both catchments.

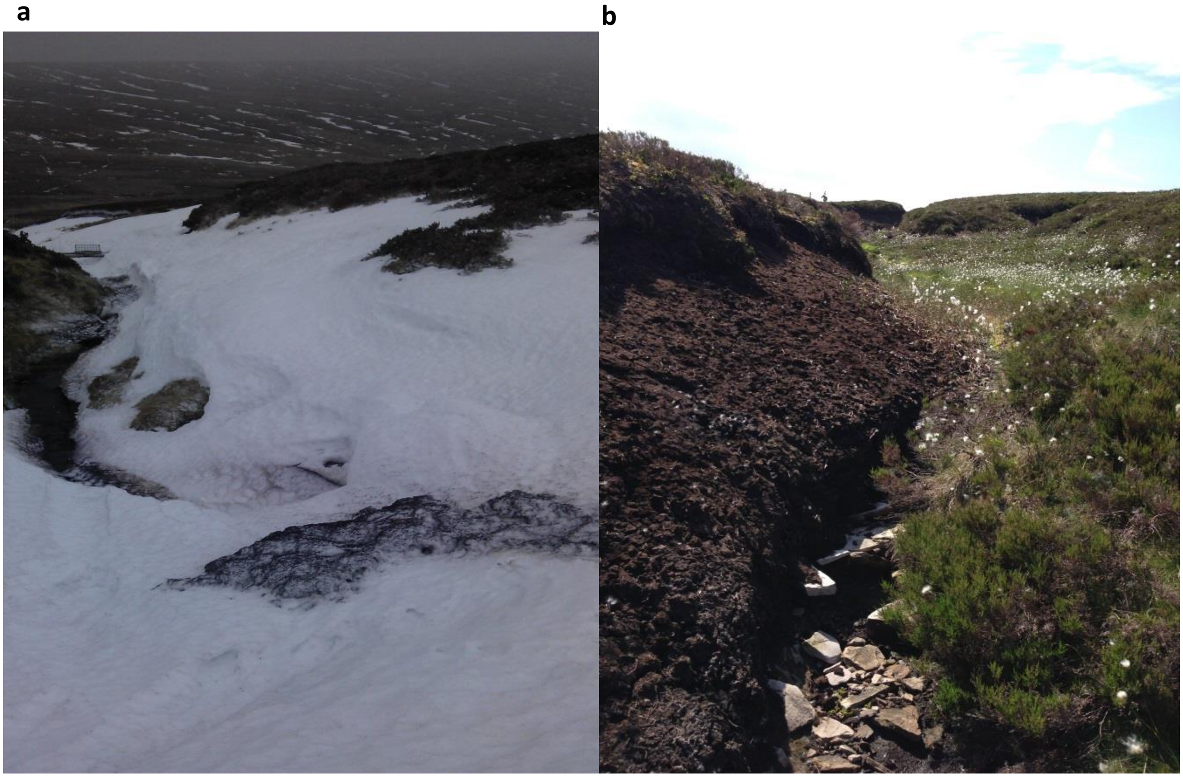

Figure 6.1: Picture of Killhope, County Durham. a) Taken in February 2013 of experimental catchment. b) Taken in June 2013 of experimental catchment.

The field management is also leads to some data gaps. As both drain blocking site and revegetation site were primarily used for grouse shooting, the visit to the site was limited during the shooting season: on average one and half months twice a year at both sites. At the revegetation site, the meteorological tower in the control catchment is located in the distance sight of a shooting butt. and therefore was taken down by the gamekeeper. The lack of the control meteorological data makes the comparisons between the evaporation and the energy budget between the catchments impossible and thus the data comparison is mainly based on the water tables in between catchments.

6.2 Overall Conclusion

This thesis is primarily focused on the impacts of a series of peat land management strategies (drain blocking and revegetation) on DOC changes. Both drain blocking and revegetation showed limited impacts on the DOC, with ranges of 2.2% – 4% change of DOC concentration observed upon drain blocking and no clear changes of DOC upon revegetation. The impacts of drain blocking on revegetation were noticed when a stable water table was achieved by drain blocking (Worrall et al., 2007). Therefore, if drain blocking and revegetation were conducted in the same study site, a joint impact of two managements could be expected.

Both drain blocking and revegetation studies indicate significant relations of site and scale difference. In other words, the same practices of both managements would have different results when applied to different sites.

Although some of the studies were conducted over 4 years periods (drain blocking), land managements of drain blocking and revegetation observed small effects over the DOC concentrations. The land management effects as such were strongly linked to changes of water table. Studies of water table changes (caused by drought or flood) observed long lasting effects even 5 years after events (Worrall et al., 2006). Therefore, longer observation periods may lead to better effects of blocking or revegetation, especially if combined studies of drain blocking and revegetation were applied, a 5-year study period would be expected.

The bank filtration study was conducted as a side project to test whether it is applicable to the UK. Results of the column study indicate bank filtration was not suitable as a water treatment if primarily focused on DOC removal in the UK as the DOC levels were at least 40 mg C g/l lower than the applied soil DOC equilibrium range of bank filtration in the UK.

6.3 Future work

Besides the data limitations described during the study, there is some further work that could be done. Column study was performed on a single column system which is flushed by deionized water in between different sets of DOC eluent. However, this may lead to inaccuracy of the comparison between control and experimental data. Therefore, an additional set of control column could be included in the study.

As various studies indicate that drain blocking would benefit the revegetation in peatland (Holden et al., 2013). A combined study of drain blocking and revegetation could be conducted to assess the effects on DOC removal and water colour changes. Also, the revegetation of land leads to the different buffer time observed during the peak flow event compared to bare peat, therefore a peak events analysis should be conducted to access the potential benefit of revegetation effects on DOC removal during the peak flow events. In terms of limitations of the revegetation study, a series of soil water dipwells were installed on the experimental catchment during May 2014 in order to trap the soil water under the extreme dry conditions of the site during the summer. However, the study periods weren't long enough for the soil water dipwell to trap enough samples, therefore a longer study periods should be carried out that could take into consideration data from these soil water traps. In case of the meteorological tower that was taken down in the control catchment, Brown et al. (2015) indicates using soil thermal regime as a tool to access the vegetation management. Therefore, an alternative soil regime comparison could be included in between catchments in the revegetation site to the comparison of energy budget between catchment.

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Appendices

The disc provided with this these contain the data of following

1. Date of drain blocking (Where the original projected conducted by E. K. Turner were included).
2. Date of events analysis.
3. Date of revegetation study.
4. Date of column bank filtration study.