Changes in fluxes of dissolved organic carbon (DOC) from small catchments in central Scotland

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Statement of Originality

I hereby confirm that this research was carried out by the undersigned and that all research material has been duly referenced and cited

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3rd April, 2008

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Abstract

Concentrations of dissolved organic carbon (DOC) measured within water bodies have been increasing on a global scale over the last two decades. Changes in temperature and rainfall have been shown to increase the production and export of DOC from catchments with peat soils in the UK (Freeman *et al.*, 2001). However it is not clear whether increases in DOC concentrations are caused by production increases induced by temperature changes or by a greater incidence of high flows induced by rainfall changes. Increases in both temperature and rainfall have been predicted in Scotland over the next few decades (Kerr *et al.*, 1999) which may further increase current DOC concentrations and exports. The implications of this include both a decrease in water quality and an increase in mobility of metals in upland water bodies.

The overall aim of the thesis is to determine if the relationship between dissolved organic carbon (DOC) concentrations and discharge has changed over a 20 year period in small stream catchments in Scotland, in order to better understand the role of hydrology, in driving changes in DOC concentration. To achieve this streams draining two coniferous forest sites and one moorland site were monitored intensively between June 2004 and February 2006. Analysis of the relationship between DOC and discharge, within the catchments, identified the importance of the amount of precipitation falling on the catchment, antecedent precipitation and season, on the concentration of DOC that was measured within the stream. Models were then developed using variables to represent these drivers in terms of both the production (seasonal sine values and 14 day average temperatures) and movement (log of discharge (log Q), days since previous storm event and rising or falling stage) of DOC. In the Ochil Hills catchment, the best predictive model, used 4 hour average discharge and 1 day average 30cm soil temperatures (R^2= 0.88). In the Duchray and Elrig catchments, the best predictive models produced used discharge and seasonal sine values; the strength of the model was greater in the Elrig (R^2= 0.80) than the Duchray (R^2= 0.48) catchment. The strength of the regression models produced highlighted the importance of precipitation in the movement of DOC to the stream and temperature variables representing production in the surrounding catchment.

To determine if dissolved organic carbon (DOC) concentrations had changed within the three study catchments, since previous research was conducted at the same sites in the early 1980s and 1990s (Grieve, 1984a; Grieve, 1994), then regression analysis conducted in the previous research was repeated, so changes in the DOC and discharge relationship could be identified. Analysis of the Ochil Hills regression equations identified higher log of discharge and lower temperature and seasonal sine values in the present study (2004-06), when compared to the previous study (1982-83). This suggests that more DOC is now available for movement from the soil, and that the difference between winter and summer DOC production has decreased, potentially because of increasing temperatures. This would explain the limited increase in DOC concentration within the Ochil Hills stream. In the Duchray and Elrig streams, a large increase in DOC was identified at all discharges when all the models produced were compared between the two sampling periods (1989-90 and 2004-06). The increasing trend in DOC concentrations is too large to have been produced by change in temperature alone and it is suggested that the measured reduction in acidic deposition has resulted in the increased DOC concentrations measured in the Duchray and Elrig. The results from this research have identified that concentrations of DOC have increased in Scottish streams over the last 20 years and that the increases in DOC have been induced, potentially by temperature changes in climate. However, changes in temperature are not the only driver of this change as the reduction in acidic deposition is potentially more important, specifically in areas with base poor geology such as the Duchray and Elrig catchments.

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Chapter 1 - Introduction

1.1 Rationale

Dissolved organic carbon (DOC) is a small, yet integral, component of the natural global carbon cycle. It is important in the supply of energy for soil microbial activity (Neff and Asner, 2001) and represents a supply of energy to heterotrophs in water bodies (Hader *et al*., 1998; Drakare *et al*., 2002). Within water bodies, DOC is a major contributor to water colour (Watts *et al*., 2001) and plays an important role in pH buffering (Hruska *et al*., 1999). Concentrations of DOC measured within water bodies have been increasing on a global scale over the last two decades. These increases in DOC concentrations have far reaching implications, which include a reduction in the global carbon store, a decrease in water quality and an increase in mobility of metals in upland water bodies. Extensive research has been conducted to identify the drivers behind the DOC increases, largely focussing on changes in climate, specifically temperature and precipitation patterns. In the UK, it has been recognised that changes in temperature and rainfall increase the production and export of DOC from catchments with peat soils (Freeman *et al*., 2001). However, it is not yet clear whether the increases in DOC concentrations are caused by production increases induced by temperature changes, or by a greater incidence of high flows induced by rainfall changes. Separation of these drivers is inherently difficult and little research conducted in this area. Despite this, the need for a separation of these factors is clear. With increases in temperature and rainfall already recorded in Scotland, and further increases predicted (Hulme *et al*., 2002), current DOC concentrations and exports may further increase. Additional factors may also be contributing to the increase in DOC concentration measured, as reductions in acidic deposition have been found to correspond to increases in DOC concentrations (Harriman *et al.,* 2001; Monteith and Evans, 2001). This study aims to address these issues and the specific aims and objectives of the project will now be outlined.

1.2 Aim

The overall aim of the project is to determine if the relationship between Dissolved Organic Carbon (DOC) concentrations and discharge has changed over a 20 year period in small stream catchments in Scotland, in order to better understand the role of hydrology in driving changes in DOC concentration.

1.2.1 Objectives

The three specific objectives of this project and the hypotheses which will be tested are as follows: -

Objective 1: Establish potential controls of dissolved organic carbon concentrations within the three study catchments.

The concentration of dissolved organic carbon (DOC) measured within water bodies is dependent both on season and the intensity and length of precipitation, as the concentration of DOC produced within the soil changes with temperature and the movement of DOC to the stream is controlled by precipitation and soil hydrology. Therefore to achieve objective 1, regular long term sampling and monitoring is required in the three catchments selected for this study, to ensure that samples are taken at a range of discharges throughout the sampling period. This will enable the identification of the controls of the production and movement of DOC within the catchments.

- ***Hypothesis 1:*** Temperature and hydrology are the main drivers of short term changes in DOC concentrations in the three streams studied.

Objective 2: Model dissolved organic carbon fluxes within the three study catchments

Temperature and precipitation will be used to produce regression relationships modelling dissolved organic carbon (DOC) concentration within the three study catchments. This will identify which variables are important in the control of DOC concentrations within the catchments.

Objective 3: Determine if dissolved organic carbon concentrations have changed within the three study catchments since previous research was conducted at the same sites in the early 1980s and 1990s.

Previous research within the catchments used in this study during the early 1980s and 1990s, developed regression relationships between DOC and a range of controlling factors affecting the concentration of DOC that was measured within the stream. To identify if the relationship between DOC and discharge has changed, the regression relationships developed during the early 1980s and 1990s, will be compared with the regression relationships developed in this study to meet objective 2.

- ***Hypothesis 2:*** DOC production has increased due to increases in temperature and/or reductions in acidic deposition since previous research was conducted at the same sites in the early 1980s and 1990s. This results in a change in the slope of the regression between DOC and discharge.
- ***Hypothesis 3:*** The slope of the DOC/discharge regression will show a greater change in the forest catchments than in the moorland catchment. Forested catchments were subject to the greatest loadings of acid deposition prior to the 1980s and therefore the greatest reduction in acidic deposition subsequently.

1.3 Structure of Thesis

The thesis has been divided into 8 chapters, chapter 1 contains a rationale for the project and the aims and objectives are discussed. Chapter 2 contains an overview of the production of dissolved organic carbon (DOC), its movement to water bodies, and potential implications of its globally increasing concentrations. Chapter 3 outlines the methods that were used in the collection of samples and the measurement of discharge and meteorological data, as well as the DOC analysis techniques. Chapters 4 – 6 presents the results collected from each of the three catchments, and discuss the results focussing on identifying the DOC controls within the catchments (objective 1). Chapter 7 develops the relationship between DOC and the controls identified in chapters 4 – 6 for each of the catchment, in order to identify the present controls of DOC within the catchment (objective 2) and to compare the regression relationships that were developed with those previously developed in previous research to determine if DOC concentrations have changed between the two sampling periods (objective 3). The final chapter is chapter 8, which will form a summary of the thesis, identifying the conclusions that can be drawn from the research and if the objectives of the study were met and hypothesis answered.

Chapter 2 - An overview of the production of dissolved organic carbon (DOC), its movement to water bodies, and potential implications of its globally increasing concentrations

Chapter 2 presents an overview of the issues that are central to this project, focussing on the mechanisms associated with the production and movement of dissolved organic carbon (DOC) to water bodies, with particular attention given to the worldwide observed increases of DOC in water bodies, the possible reasons behind these increases and potential implications.

2.1 The carbon cycle

Carbon provides the basic building blocks for all life on earth, and the natural carbon cycle shown in Figure 1 is one of the most important of the global cycles. The principal fluxes of carbon in the natural carbon cycle, are between the atmosphere and ocean (90 PgC/yr), and the atmosphere and land (120 PgC/yr), which are approximately balanced each year (Intergovernmental Panel on Climate Change (IPCC), 2001).

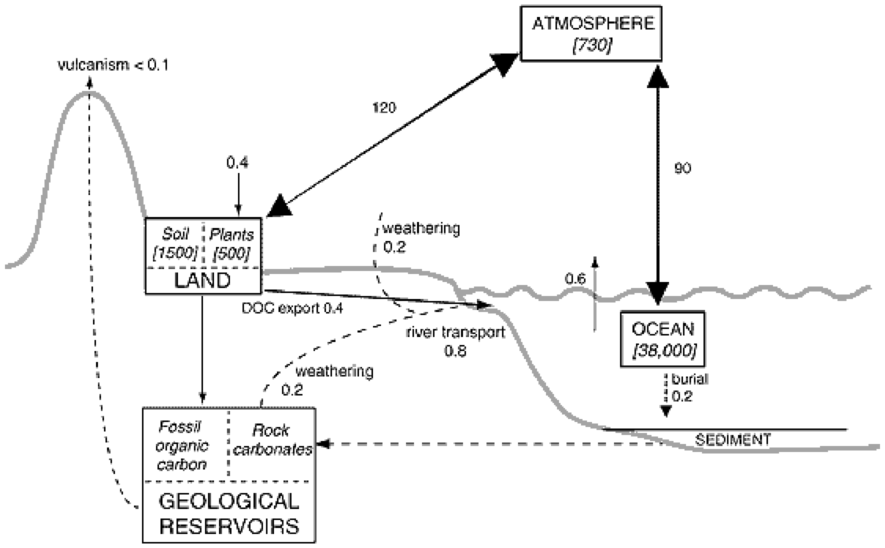


Figure 1: The main components of the natural global carbon cycle: The thick arrows show the gross primary production and respiration by the land biomass and the physical exchange between the air and sea. The thin arrows represent additional natural fluxes, with the dashed thin line denoting the fluxes of $CaCO_3$. All the fluxes shown are measured in PgC/yr (Intergovernmental Panel on Climate Change (IPCC), 2001).

2.1.1 The role of soil and plants in the carbon cycle

The land is a store for 2000 PgC, which is split between the soil and plants. 500 PgC is stored by plants, which assimilate 120 PgC/yr from the atmosphere for use in photosynthesis (Intergovernmental Panel on Climate Change (IPCC), 2001). This CO_2 flux is returned to the atmosphere via respiration by plants (60 PgC/yr), heterotrophic respiration (55 PgC/yr), and direct oxidation in fires (4 PgC/yr) (Intergovernmental Panel on Climate Change (IPCC), 2001). The soil is a large sink for carbon, storing perhaps two or three times more carbon than is found in the atmosphere as CO_2 (Davidson *et al*., 2000). The estimates of this organic carbon store, in the top 100cm of soil, have ranged from 1395 Pg (Post *et al*., 1982) to more recent estimates of 1462–1548 Pg (Batjes, 1996) and 1500 Pg by the Intergovernmental Panel on Climate Change (Intergovernmental Panel on Climate Change (IPCC), 2001). In the United Kingdom, estimates of carbon in the soil have also varied, with the most recent estimate by Milne and Brown (1997) of 9.8 Pg (± 2.5 Pg). Scottish soils hold a large proportion of the UK carbon store, and estimates of the sink of carbon in Scotland have ranged from 19 Pg (Howard *et al*., 1995) to a more recent estimate of 7 Pg (Milne and Brown, 1997). The carbon that contributes to this large but active soil store initially joins the detritus pool, where it either quickly decomposes and is respired by heterotrophs, or is converted to modified soil carbon (humus) which takes longer to decompose and respire. A further small fraction of the modified soil carbon is resistant to decomposition, this along with the black carbon produced in fires makes up the inert carbon pool (Intergovernmental Panel on Climate Change (IPCC), 2001). A major soil store of carbon is peat, accumulating as a result of the slow decomposition processes that occur within peat (Grieve and Marsden, 2001). It has been estimated that within the top 100 cm, peat is a global sink for 330 Pg of carbon (Batjes, 1996). In Scotland, carbon held within peatlands has been estimated to be 4.3 Pg (Milne and Brown, 1997). The large sink of carbon found within Scottish peatlands, represents a large potential source of dissolved organic carbon (DOC), the availability of which will be examined within this project.

2.1.2 Anthropogenic modification of the carbon cycle

The natural carbon cycle has however been detrimentally altered by human activity through increasing emissions of CO_2 from the burning of fossil fuels (5.3 PgC/yr), cement production (0.1 PgC/yr) and land use change (1.7 PgC/yr), all contributing to the increasing CO_2 concentrations measured within the atmosphere (Intergovernmental Panel on Climate Change (IPCC), 2001). Indeed, changes in land use have been identified to have contributed a net flux of 124 PgC to the atmosphere between 1850 and 1990 (Houghton, 1999); the flows to the atmosphere are primarily from forests as a result of wood harvesting (108 PgC) and from the conversion of forests to agricultural lands (105 PgC), other factors contribute to a smaller extent to this flux, which totals 373 PgC. This figure is then balanced with the carbon that accumulates within the forest and the fallows of shifting cultivation (249 PgC) to produce the net flux of 124 PgC (Houghton, 1999).

The location of the sinks of these new CO_2 sources are however harder to identify. The IPCC (2001) identified further land (1.9 PgC/yr) and ocean (1.9 PgC/yr) sinks of carbon. Yet, this does not account for all the excessive carbon produced; various hypothesis have been put forward to explain this mysterious missing sink, including further uptake by the oceans or the northern temperate forests, while other ecosystems such as boreal forests, northern peatlands and wetlands could also be playing a role (Schindler, 1999). Indeed, the increases in atmospheric CO_2 concentration may not be balanced with the capacity of the sinks to absorb this excess carbon. Identification of carbon sinks and monitoring of carbon fluxes, are therefore of vital importance to understand the influences of human activity on this cycle.

2.1.3 Dissolved inorganic and organic carbon fluxes

Dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) are small, yet important components of the global carbon cycle. The export of DOC, from soils and plants to rivers and oceans, accounts for a flux of 0.4 PgC/yr, which is subsequently respired and released to the atmosphere (Intergovernmental Panel on Climate Change (IPCC), 2001). DIC is produced within the soil, through the weathering of carbonate minerals, principally calcium carbonate ($CaCO_3$), also dolomite ($MgCO_3$) (Batjes, 1996). When this weathered material is transported to water bodies, it is measured as dissolved inorganic carbon (DIC) comprising bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions, and dissolved CO_2 (Vogel *et al*., 2000). 0.4 PgC/yr of DIC is exported from the soil to rivers, and then the oceans, half of which is returned to the atmosphere during $CaCO_3$ production by marine organisms, the remaining half is buried in deep sea sediments (Intergovernmental Panel on Climate Change (IPCC), 2001).

2.2 Dissolved organic carbon (DOC)

The flux of dissolved organic carbon (DOC) from the soil and plants to the rivers and oceans, may be small (0.4 PgC/yr) (Intergovernmental Panel on Climate Change (IPCC), 2001), but the roles DOC performs within each of these components is essential. Within the soil, fluxes of DOC are a relatively large source of carbon for microbial activity (Neff and Asner, 2001). The soil also supplies a large proportion of DOC to water bodies where DOC is critical in the provision of energy for heterotrophs (Hader *et al*., 1998; Drakare *et al*., 2002) and pH buffering (Hruska *et al*., 1999). The concentration of DOC within the water body can also alter its colour (Watts *et al*., 2001) and the depth that ultraviolet (UV) radiation penetrates within the water body (Hader *et al*., 1998). To further highlight the essential role that DOC plays within the carbon cycle, the following sections will define DOC; identify sources of DOC to water bodies and functions of DOC within the water bodies.

2.2.1 Definition of DOC

Dissolved organic carbon (DOC) has been defined as the fraction of total organic carbon (TOC) in water that passes through a 0.45 µm filter (Vogel *et al*., 2000; McDonald *et al*., 2004). This definition has not however been strictly adhered to within the literature; water samples have been filtered using a range of filter pore sizes or not filtered at all and when the filtrate is analysed the resulting concentrations are defined as DOC. In Hope *et al.'s* (1997) study of DOC export from 85 British rivers, samples were not filtered prior to analysis, as it was identified in the majority of cases that the difference between DOC concentration measured in samples that were filtered and unfiltered was less than 5%. Similarly, Dawson *et al.* (2001b) deemed that it was not necessary to filter samples taken from a Scottish headwater stream, due to the negligible concentration of particulate organic carbon in the water. Baker and Spencer (2004) used GF/C (1.2 µm) filters to filter samples from the River Tyne, but GF/F (0.7 µm) filters to filter their River Tyne estuarine water samples. In Tipping *et al.'s* (1988) study of DOC concentrations in Cumbrian lakes and streams, samples were filtered using GF/F filters, which were also used in Ford *et al.'s* (1990) study of DOC concentrations in the Moisie River Quebec, whilst Fraser (2001) used 0.45 µm filters to filter samples from the Mer Bleue bog, Ontario, Canada. The varying filter papers used within these studies illustrates the potential difficulties in comparing DOC concentrations between different studies. Within this study, samples will be filtered using GF/C filters which were used in the previous studies (Grieve, 1984a; Grieve, 1994), with which the measurements from this study will be compared.

2.2.2 Sources of DOC

The concentration of dissolved organic carbon (DOC) that is measured within a water body consists of organic carbon inputs from both external and internal sources. A summary of the organic carbon fluxes, and their individual contributions to the total organic carbon flux, is shown in Table 1. These inputs can be separated into three groups depending on their size and include coarse particulate organic matter (CPOM, > 1mm in diameter), fine particulate organic matter (FPOM, <1mm in diameter) and dissolved organic matter (DOM), 50% of which is assumed to be DOC (Grieve, 1984b). Only a small fraction of DOC is produced within the water body: sources include DOC leached from leaves, larger particulate organic matter (POM) that is broken down and extracellular releases from plants (Allan, 2001). The majority of the DOC comes from sources external to the water body, primarily the soil and groundwater. Concentrations of DOC within the groundwater are generally low (Easthouse *et al.*, 1992; Allan, 2001). However, the soil is a large store of organic matter which includes the living biomass (micro-organisms and intact plant and animal tissues), the residues of plants that are beginning to be decomposed by microbes (detritus), and after further microbial decomposition, organic substances which can no longer be recognised as tissues (soil humus) (Brady and Weil, 1999). This large store of carbon ensures high concentrations of DOC are available to move from the soil to the water bodies via a range of hydrological pathways including surface flow and sub-surface flow which are shown in Table 1 and will be further discussed in section 2.3.3.2.

Table 1: Sources of organic matter to running waters. The majority originates from outside the water body, the sources marked with an asterisk, is energy fixed by photosynthesis within the water bodies that then enters heterotrophic pathways (after Allan (2001)).

Sources of Input	Comments
Coarse Particulate Matter (CPOM)	
Leaves and Needles	Major input in woodland streams, typically pulsed seasonally
Macrophytes during die-back	Locally important
Woody debris	May be major biomass component, very slowly utilized
Other plant parts (flowers, fruit, pollen)	Little information available
Other animal inputs (faeces and carcases)	Little information available
Fine Particulate Organic Matter (FPOM)	
Breakdown of CPOM	Major input where leaf fall or macrophytes provide CPOM
Faeces of small consumers	Important transformation of CPOM
From DOM by microbial uptake	Organic microlayers on stones and other surfaces
From DOM by physical-chemical processes	Flocculation and adsorption, probably less important than microbial uptake route.
Sloughing of Algae*	Of local importance, may show temporal pulses
Sloughing of organic layers	Little information available
Forest floor litter and soil	Influenced by storms causing increased channel width and inundation of floodplain, affected by overland *versus* sub surface flow
Stream bank and channel	Little known, likely related to storm events
Dissolved Organic Matter (DOM)	
Groundwater	Major input, relatively constant over time, often highly refractory
Sub-surface flow or interflow	Less known, perhaps important during storm events
Surface flow	Less known, perhaps important during storm events
Leacate from detritus of terrestrial origin	Major input, pulsed depending upon leaf fall
Throughfall	Small input, dependent on contact of precipitation with canopy
Extracellular release and leachate from algae*	Of local importance, may show seasonal and diel pulses
Extracellular release and leachate from macrophytes*	Of local importance, may show seasonal and diel pulses

2.2.3 Composition of DOC

Compositionally, DOC can be defined as having two components, the humic and the non-humic fraction. The non-humic fraction (10 - 25% of DOC) consists of molecules that have an identifiable structure including carbohydrates and fatty, amino and hydroxyl acids (Allan, 2001). The humic fraction has been estimated to contribute between 50 and 75% (up to 90% in strongly coloured waters), of the total DOC concentration (Allan, 2001) and has been described as being amorphous, brown or black in colour and polydisperse (Janos, 2003). The humic substances can be further fractionated according to their hydrophobic and hydrophilic properties, into hydrophobic and hydrophilic acids, base and neutral fractions which are shown in Figure 2. The abundance of each of these fractions within a water sample varies according to the source of the DOC. For instance, Easthouse *et al.* (1992) analysed soil solution (podzols and peat) and stream samples from the Birkenes catchment, Southern Norway for their hydrophobic and hydrophilic fractions. They found that the hydrophobic and hydrophilic acid fractions dominated within the soil and stream samples, accounting for 90% of the total DOC, with the remaining fractions found in small amounts. This fractionation of the humic substances was used successfully by Easthouse *et al.* (1992), to identify where the DOC measured within the brook originated within the soil. They achieved this through the use of end-member mixing analysis (EMMA) which determines the combination of soil environments (end-members), which may explain the chemistry of the stream under changing hydrological conditions. This led them to identify that during base flow conditions the origin of the DOC was from the deeper bog layers surrounding the brook, because of the combination of low hydrophobic and hydrophilic acids and high hydrophilic bases that were measured. However, during peak flows the B horizon and surface bogs became the major contributors (Easthouse *et al*., 1992).

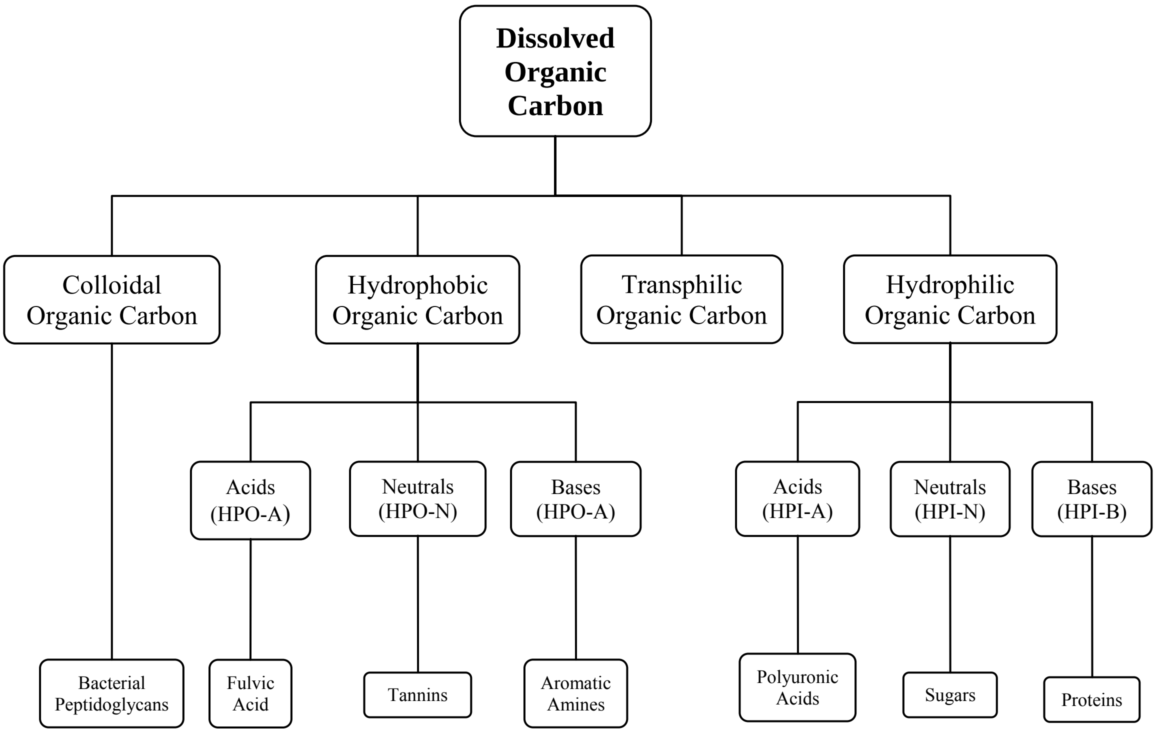


Figure 2: DOC fractionation diagram (after Leenheer (2004)

DOC can also be fractionated into compounds e.g. tannins and sugar (Figure 2), to gain additional information about the source of DOC. Fractionation of DOC was used by Leenheer (2004) to determine the sources of DOM to Anaheim Lake, California. They identified that the major DOM precursor in the samples was the oxidative degradation of amino sugars (derived from bacterial cell walls) to N-acetyl hydoxy acids, which would be indicative of a primarily autochthonous (algae and bacteria) source within the lake (Leenheer, 2004). The knowledge of the composition of the DOC can also be used in the design of water treatment processes, as DOC fractions react differently to water treatment processes, for instance amino acids produce low yields of regulated disinfection by-products (DBPs) when chlorinated, but tannins produce a high yield of DBPs (Leenheer, 2004).

2.2.4 Functions of DOC within water bodies

Dissolved Organic Carbon (DOC) has been identified as an integral component of the global carbon cycle; its functions within the cycle and specifically in water bodies are wide ranging. The movement of DOC from the soil to water bodies is essential in the provision of energy for heterotrophs (Hader *et al*., 1998; Drakare *et al*., 2002). In water bodies (Drakare *et al*., 2002), adsorption of UV-B radiation breaks down high molecular weight DOC through photolysis into simpler DOC molecules including formaldehyde, acetaldehyde, glyoxylate and pyruvate, which are then available for bacterioplankton which remineralize the carbon for use by other organisms (Hader *et al*., 1998). DOC also protects water organisms from harmful UV radiation, as the concentration of DOC determines how much light penetrates through the water. Excessive UV radiation may decrease biomass productivity resulting in reduced food production for human consumption, reduced CO_2 sink and changes in species composition (Hader *et al*., 1998). DOC is also important in pH buffering, by moderating the effects of mineral acid inputs from acid deposition, which increase the acidity of the water (Hruska *et al*., 1999). The concentration of DOC within a water body will also alter its colour (Watts *et al*., 2001), and high concentrations of DOC are responsible for the brown coloured water that can be seen in streams draining peaty catchments. Indeed, the long term mean concentration of DOC, has been identified to be highly correlated with long term mean water colour in streams and lakes (Molot and Dillon, 1997). The colour of the water changes throughout the seasons, due to the availability of DOC with higher concentrations, and as a result darker colour, measured in the autumn and winter than the spring and summer (Watts *et al*., 2001). The presence of high concentrations of DOC within stream water not only has implications for the stream biota, but also for humans as 70% of the United Kingdom's water resource is derived from upland catchments with peatland areas (Watts *et al*., 2001). Coloured water is not thought to be a health risk, but the water has to be treated by the water companies, or the public would not drink it. The treatment process of chlorinating coloured water to reduce risk of bacterial infections is however thought to produce carcinogens, principally trihalomethanes (Watts *et al*., 2001).

2.3 Differences in production and movement of DOC between catchments

The annual dissolved organic carbon (DOC) export measured in a range of catchments from around the world is shown in Table 2. Here it can be identified that there is a large variation in DOC export between catchments. Amongst the lowest DOC exports are from the Subarctic and tropical forest catchment, these catchments are however not relevant to sites monitored in this study, so this discussion will focus on the humid temperate systems where DOC exports are greater. If we examine a selection of these sites more closely, looking at the range of individual concentrations of DOC, dramatic differences can be seen. In the Brocky Burn peatland catchment, DOC concentrations ranged from 5.78 to 41 mg l^{-1}, with an average concentration of 14.5 mg l^{-1} (Dawson *et al*., 2002). In a second peatland catchment, the Upper Hafren, DOC concentrations were much lower ranging from 1.40 to 5.88 mg l^{-1}, with an average concentration of 2.88 mg l^{-1}, giving it a lower yearly export (Dawson *et al*., 2002). The Maimai temperate evergreen forest produced a greater average DOC concentration (4.5 mg l^{-1}) than the Upper Hafren site, but a lower yearly export (Moore, 1989) and the Hubbard Brook, temperate deciduous forest site had average concentrations of ~2-3 mg l^{-1} (McDowell and Likens, 1988), similar to the Upper Hafren site, but nevertheless also had a lower yearly export because of a lower throughput of water. This is only a small selection of sites, but it highlights the large difference in DOC concentrations that are produced both annually and during individual sampling events. This suggests, that to identify why the DOC export differs between catchments, it is necessary to understand the processes that are integral to its production and movement from the surrounding catchment; which include the catchment's soil carbon store, vegetation, and local climate. These factors will be discussed in the following sections, with specific focus on how DOC exports differ between forested and moorland catchments such as those in this study.

Table 2: DOC exports (g C m^{-2} yr^{-1}) and annual mean precipitation (mm) from a range of catchments

Site	**Catchment Type**	**DOC export (g C m^{-2} yr^{-1})**	**Annual mean precipitation (mm)**	**Reference**
Granger Basin, Yukon, Canada	Subarctic	1.64	270	Carey (2003)
Hubbard Brook, New Hampshire, USA	Temperate Deciduous Forest	2	1310	McDowell and Likens (1988)
Luquillo Mountains, Puerto Rico	Tropical Evergreen Forest	3.25	3500	McDowell (1998)
Troutbeck catchment, Moorhouse, UK	Upland Peat	4 - 7.4	1953	Worrall *et al.* (2006b)
Maimai, Westland, New Zealand	Temperate Evergreen Forest	6.8	2400	Moore (1989)
Ochil Hills, Scotland	Upland Peat	8	1200-1500	Grieve (1984a)
Mer Bleue bog, Ontario, Canada	Bog	8.3	910	Fraser *et al.* (2001)
Upper Hafren, Wales	Upland Peat	8.4	2726	Dawson *et al.* (2002)
Loch Ard, Burn 11, Scotland	Temperate Evergreen Forest	15	2000-2500	Grieve (1994)
Loch Ard, Burn 10, Scotland	Temperate Evergreen Forest	16	2000-2500	Grieve (1994)
Brocky Burn, Scotland	Upland Peat	16.9	1164	Dawson *et al.* (2002)
Larry River, Westland, New Zealand	Wetland (Moss/fern/scrub vegetation)	65.1	2500	Moore and Jackson (1989)

2.3.1 DOC retention and release in soils

The largest potential source of dissolved organic carbon (DOC) for water bodies is the soil in the surrounding catchment (Aitkenhead *et al.,* 1999; Kalbitz *et al.,* 2000; Billett *et al.,* 2006). The concentration of DOC that is however available from the catchment varies according to soil type. Catchments with a high proportion of organic soil represent a large potential source of DOC to water bodies. In catchments containing peat, where carbon accumulates because of low decomposition rates (Grieve and Marsden, 2001), the percentage peat cover has been found to be a good predictor of stream water DOC concentration (Dillon and Molot 1997; Aitkenhead *et al.,* 1999). High exports of DOC were measured in the peatland catchments shown in Table 2 (Dawson *et al*., 2002; Worrall *et al*., 2006b) and also for the Ochil Hills catchment used within this study, which has soils which include hill peats, peaty gleys and peaty podzals (Grieve, 1984b). Many forest catchments in the UK have also been planted on drained peatlands, with soils that have a high organic content, and are potentially a large source of DOC (Hargreaves *et al*., 2001); an example of this is the two Loch Ard temperate evergreen catchments shown in Table 2 and used within this study, both of which had high DOC exports (Grieve, 1994) although one site has a higher percentage of mineral soils. Concentrations in the forest sites may be further increased due to the leachate from the leaf litter layers where high concentrations of DOC are measured (Hongve, 1999) as well as the underlying humus (McDowell and Likens, 1988), which together have been identified as the largest DOC sources in soil (Kalbitz *et al.,* 2000).

In catchments that have a larger proportion of mineral soils, and also in the mineral horizons of any catchment, concentrations of DOC are lower than in the organic horizons (Easthouse *et al*., 1992; Moore *et al.,* 1992; Kalbitz *et al*., 2000). Concentrations of DOC decrease with depth, initially because of metabolization by micro-organisns (Allan, 2001), but in the mineral horizons particularly the B horizon, DOC is adsorbed to metals, predominantly iron (Fe) and aluminium (Al) oxides and hydroxides (McDowell and Wood, 1984; Jardine *et al.*, 1989; Moore *et al.*, 1992). Moore *et al* (1992) identified the importance of soil in the adsorption of DOC, through the determination of sorption isotherms for 48 soil samples (collected from 20 profiles with low organic carbon contents from 0.1 to 4.3%). The sorption isotherms were produced by plotting the initial DOC concentration that was added to each soil (seven DOC solutions ranging from 0 to 81 mg l^{-1}), against the change in DOC concentration (sorption per mass of soil) after the soils were equilibrated with the added DOC solutions, to produce a linear regression, which effectively described the isotherm relation for 46 of the soil samples. The DOC_{np} (null point) concentration, where the net sorption was zero, was then calculated from the sorption regressions. Using partial regression analysis, it was identified that there was a significant positive relationship between the DOC_{np} concentration and the soil organic carbon, and a significant negative relationship between the DOC_{np} and both oxalate-extractable aluminium (Al_o) and dithionite extractable iron (Fe_d) (Moore *et al.*, 1992). The regression analysis shows that DOC_{np} adsorption increases when there are higher Al_o and Fe_d concentrations in the soil and decreases when there are higher organic carbon concentrations. Indeed, 70% of the variation in DOC_{np} was explained by these variables in a multiple regression model (Moore *et al.*, 1992). Moore *et al.'s* (1992) study examined the DOC sorption processes over a 48 hour period (>90% of sorption occurred in the first 24 hours), yet in a longer term (1 year) study by McCracken *et al.* (2002), it was identified that microbial decomposition was also important. In McCracken *et al.'s* (2002) study, soil columns (all nearly 100% mineral soils, with little or no organic content) were leached with three different concentration solutions of DOC. In the soils leached with the highest concentration DOC solution, only 50% of the DOC lost from solution was subsequently measured as soil organic carbon at the end of the experiment, suggesting the importance of microbial decomposition (McCracken *et al.*, 2002). DOC can also adsorb to clay minerals, as Jardine *et al.* (1989) found, when the Fe in their loamy soils was experimentally removed and significant quantities of DOC were still absorbed to the soil. Soil water pH has also been found to be important within adsorption processes, Jardine *et al.* (1989) found that the maximum adsorption of DOC within their loamy soils occurred at ~ pH 4.5.

The carbon that has been adsorbed can also be released via desorption processes, and numerous studies have been conducted to investigate the processes that are associated with carbon desorption. Münch *et al.* (2002) experimentally investigated the influence of varying flow regime, and chemical composition of the inflow solution on the release of carbon from forest mineral soils. They concluded that the processes important for carbon desorption were principally the solubilisation of colloidal organic matter that is only weakly attached to the mineral soil, and the desorption of carbon from the soil matrix when the soil solution pH increases (Munch *et al.*, 2002). Another study, by Christ and David (1996) investigated how the concentration of DOC desorbed from the soil changed according to the concentration of DOC that was in the soil water, as they theorised that if DOC is only stored within the soil water, then experimental addition of DOC would not affect the amount added by the soil during the extraction. However if DOC is also adsorbed to the soil, then DOC in an extractant would inhibit the dissolution of additional material (Christ and David, 1996). To identify if was the case, they performed a laboratory experiment where they added a series of DOC solutions either containing soil extracts (of differing DOC concentrations) or a DOC solution made from hydrophobic acids to their soil samples; subsequent to each addition, the soil water was extracted for analysis. They found that different fractions of DOC may have different controls on its solubility, as it was only the dissolution of the hydrophobic acids that was inhibited by the concentration of hydrophobic acid already in solution (Christ and David, 1996). However, Gu *et al.* (Gu 1994) investigated desorption of DOM from Fe oxides and identified that 72 to 92% of the DOM was irreversibly bound. The amount of absorption and desorption of DOC that occurs within a catchment will change according to the soil within the catchment. For instance, in table 2 it can be observed that the catchment with the greatest yearly DOC export (65.1 g C m^{-2} yr^{-1}) was the Larry River, wetland catchment. The average concentration of DOC, measured within the stream draining the catchment was 43.4 mg L^{-1}, one of the reasons behind such a high concentration was the inability of the subsoils to adsorb DOC (Moore and Jackson, 1989), showing the important role that soil plays in the retention of DOC. The catchments soil type therefore plays an important role in the concentration of DOC that is available for export within the catchment, whereby in catchments with organic soils, larger stores of DOC are available for export than in catchments with a larger percentage of mineral soils.

2.3.2 Catchment vegetation and DOC

The type of vegetation within a catchment plays a major role in controlling the concentrations of DOC measured within the catchment (Neff and Hooper, 2002). The type of vegetation will determine the quantity and quality of litter input into the catchment and thus the available substrate for decomposition. Vegetation type also influences the decomposability of the litter, due to its biochemical properties and to the types of microbial decomposers associated with the vegetation. Vegetation can also alter soil drainage, aspect or microclimate, again influencing carbon storage (Neff and Hooper, 2002). The catchments used in this study were two coniferous forest catchments and a moorland catchment, the influence of the vegetation on DOC concentration will therefore differ between the catchments. Typically forest catchments have been shown to produce higher concentrations of DOC than moorland catchments (Aitkenhead *et al.,* 1999; Grieve and Marsden 2001) The reasons behind these differences can be seen when focussing on the land use within the catchment and specifically the vegetation.

In forest catchments, in comparison to moorland catchments, large amounts of leaf litter are produced, which is a large source of DOC. However, concentrations of DOC measured within forest catchments, vary according to the species of trees, as can be seen in Table 2, where it is shown that the temperate deciduous forests, produces lower concentrations of DOC (McDowell and Likens, 1988) than both the tropical (McDowell, 1998) and temperate evergreen forests (Moore, 1989; Grieve, 1994). Although only a small selection of studies are discussed, it has been identified that one reason behind these differences is that evergreen trees such as those that were monitored in this study, shed their leaves continuously throughout the year, and deciduous trees shed their leaves during the autumn, thus producing different DOC concentrations throughout the year (Hongve, 1999). When peatlands are drained and forests planted, then aeration of the soil increases (Prévost *et al.,* 1999), and the number of soil animals and the species structure of the soil animals changes (Silvan *et al.,* 2000), resulting in a loss of soil carbon and potentially more DOC production.

Anthropogenic disturbance of catchments, often specific to vegetation type, can also alter DOC concentrations. Within forest catchments, the felling of trees can increase DOC concentrations (Cummins and Farrell, 2003). The acidity of the soil within a catchment will also play a major role in the concentration of DOC that is moved to water bodies, as acidity influences the solubility of DOC (Chapman *et al*., 2005). When stream water acidities have been compared between catchments, they have been observed to be greater in streams draining forested catchments than those draining moorland catchments (Harriman and Morrison, 1982; Grieve, 1990b; Harriman *et al*., 2001). This greater acidity is due to the ability of the coniferous trees to collect pollutants, including marine salts and sulphur and nitrogen compounds, which are concentrated as they pass through the forest canopy to the forest floor (Harriman and Morrison, 1982). Although differences in soil and stream water acidity exist between catchments, recent reductions in anthropogenic acidic deposition appear to correlate well with increased DOC concentrations (Harriman *et al*., 2001; Monteith *et al*., 2001); these trends will be further examined and discussed in section 2.4.4.

2.3.3 Climate and DOC

Climatic conditions at a site are integral to the concentration of DOC that is produced. The production of DOC within the soil, is directly linked with temperature (Andersson *et al*., 2000; Andersson and Nilsson, 2001; Neff and Hooper, 2002), and implications of temperature changes for DOC production under climate change scenarios will be discussed in section 2.4.1. The movement of DOC, from the soil to water bodies, is primarily controlled by water movement. The relationship between DOC, precipitation and subsequent discharges will be discussed in the following section.

2.3.3.1 Precipitation and DOC

The amount of precipitation that falls on a site has a considerable influence on the concentration of DOC that is measured within a catchment, as water is the principal driver behind DOC movement from the soil to water bodies. To understand its importance, we can examine the precipitation and subsequent yearly DOC export from the catchments in Table 2. Here we can observe that the Subarctic catchment had both the lowest annual precipitation (270 mm) and lowest yearly DOC export (1.64 g C m^{-2} yr^{-1}) (Carey, 2003). This is primarily because this catchment was covered in snow a substantial amount of the year during which DOC accumulated and was then flushed from the soil during the spring snow melts, when *ca* 67% of the DOC was exported over a 6 week period (Carey, 2003). The relationship between DOC and precipitation within the other catchments is, however, more complicated, within the three upland peat sites for example, precipitation and DOC export were high in all three catchments, but the Brocky Burn catchment which had the lowest annual precipitation (1164 mm) also had the highest yearly DOC export (16.9 g C m^{-2} yr^{-1}). It is suggested, that this is because all upland peat catchments have a large store of carbon, but the quantity of DOC released is limited by low decomposition rates, due to the low temperatures and high precipitation rates typically found within upland catchments (Grieve and Marsden, 2001). Increased concentrations of DOC are produced in peatlands under low rainfall conditions, when the depth of the acrotelm increases, increased decomposition within the upper peat layer occurs (Bragg and Tallis, 2001).

2.3.3.2 Hydrological flowpaths and DOC

Precipitation has been identified as an important driver of DOC export to water bodies. However, the hydrological flowpaths that the water follows to reach the water body (Figure 3) can control the concentration of DOC that is exported. It is shown in Figure 3 that when precipitation falls in a catchment, unless it is evaporated from the land or transpired from vegetation, it will either fall directly onto a water body (channel precipitation), flow over the surface of the land until it reaches a water body (surface flow) or infiltrate into the soil (infiltration). The soil flowpaths (surface flow and infiltration) are the greatest source of DOC to water bodies, and the flowpath which is followed is dependent on the intensity and length of the rainfall, and the time period since the previous rainfall (Worrall *et al.*, 2002). These flowpaths along with the interception of precipitation by vegetation and its subsequent runoff will be discussed in the following sections.

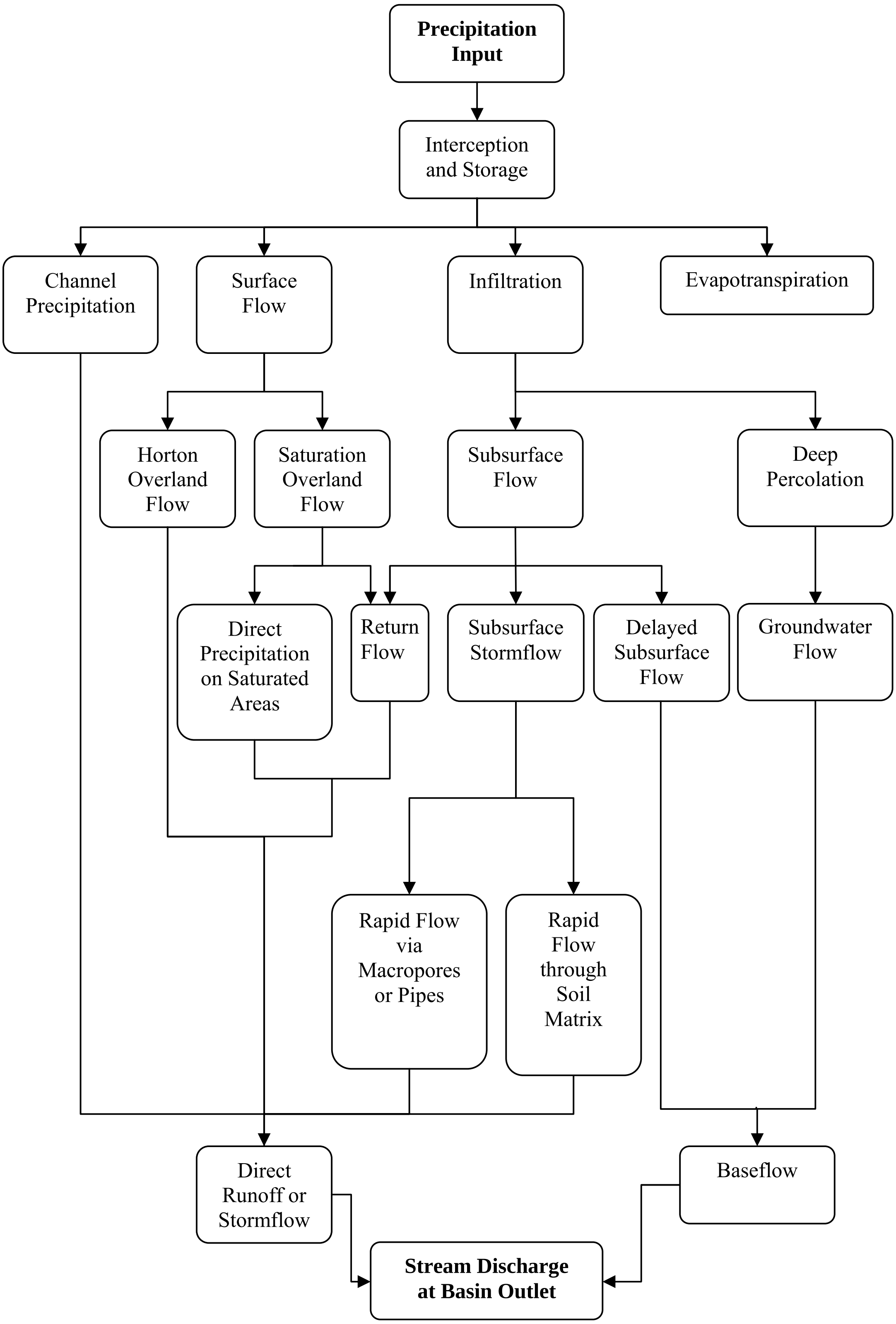


Figure 3: Schematic diagram of the runoff process (after Knighton (1998))

1) Channel precipitation

When precipitation falls, it may fall directly on the water body. Concentrations of DOC within rainwater vary between catchment, but are generally low. In a Subarctic Fen in Canada, concentrations between ~ 1-2 mg C l^{-1} were measured (Koprivnjak and Moore, 1992). Peak DOC concentrations of 4.2 mg C l^{-1} were measured in the Plynlimon catchment in mid-Wales between 1983 and 2002 (Neal *et al*., 2005) and 10.2 mg C l^{-1} in the Moor House upland peat catchment between 1993 and 2001 (Worrall *et al.* 2006a). However, DOC concentrations were generally lower in these catchments, and in the Plynlimon catchment the average DOC concentration was 0.69 mg C l^{-1} (Neal *et al*., 2005).

2) Interception by vegetation

The rainwater may also be intercepted by vegetation, where it either evaporates from the leaf surface or runs off as stem flow or throughfall. Vegetation also takes up water from the soil, which is subsequently transpired back into the atmosphere. The concentration of DOC, which runs off the vegetation, is dependent on the vegetation type. In a subartic fen catchment Koprivnjak and Moore (1992) measured 50 mg C L^{-1} in tree throughfall, 150 mg C L^{-1} in tree stemflow and 30 mg C L^{-1} in the leachate from surface mosses and Lichens. In the Plynlimon catchment in mid-Wales, throughfall and stemflow were collected from Spruce trees (Neal *et al*., 2005) and the carbon concentrations in the throughfall ranged from 0.9 to 214 mg C l^{-1} and in the stemflow from 1.6 to 128 mg C l^{-1} (Neal *et al*., 2005). However, the high concentrations of DOC measured in the throughfall and stemflow were only found in low catch volumes. It is therefore suggested that the contributions of these sources to the overall carbon flux within a catchment is limited, other limiting factors include the areal extent of the throughfall and insignificant amounts of stemflow (Koprivnjak and Moore, 1992).

3) Infiltration

If the water infiltrates into the soil, it can then reach the water body via a range of hydrological pathways. The hydrological pathway that is followed, will determine the concentration of DOC that is measured, as the available concentration of DOC alters with soil horizon, where higher concentrations would be available in the litter layers and upper organic horizons (McDowell and Likens, 1988; Hongve, 1999) than the mineral horizons (Easthouse *et al.*, 1992; Kalbitz *et al.*, 2000; Moore *et al.,* 1992),

Water which percolates through the soil to the groundwater, eventually reaches the stream via groundwater flow through the zone of saturation (Ward and Robinson, 1990) to produce the base flow within the stream. During periods of no precipitation, it is this base flow that primarily controls the DOC concentration that is measured within the stream. Concentrations are typically low (Boyer *et al.*, 1997) as the concentration of DOC usually decreases as it moves through the soil due to metabolization by soil micro-organisms (Allan, 2001) and sorption processes (Easthouse *et al.*, 1992). Soils with a higher percentage of mineral soils would therefore be expected to have lower groundwater DOC concentrations, as increased sorption of DOC in the soil would occur.

Water can also move laterally through the upper soil horizon either as unsaturated flow or more typically as shallow perched saturated flow above the main groundwater level (Ward and Robinson, 1990). This flow pathway is defined as subsurface storm flow (Figure 3) or throughflow. This type of flow occurs when the lateral conductivity in the surface horizons of the soil is considerably greater than the overall vertical conductivity through the soil profile. Therefore during a storm event, the water will enter the upper part of the profile more rapidly than it can pass vertically through the lower part, thus escaping laterally and forming a perched saturated layer (Ward and Robinson, 1990). Initial concentrations of DOC are high during storm events as the precipitation has raised the water table and water is moving through the organic rich upper soil horizons (Soulsby, 1995; Worrall *et al*., 2002;). However, if there is prolonged precipitation, DOC concentrations in the organic upper horizons could be depleted (Worrall *et al*., 2002), leading to a reduction in DOC in the stream.

Within the soil water can also move rapidly through macropores or pipes which include old root channels, cracks and earthworm or other animal burrows (Boissier and Fontvieille, 1995). This was identified to occur during storm events by Boissier and Fontvieille (1995), who simulated high intensity rainfall events in two forest soils, and found that during such events the seepage waters flowed through macropores. However, the concentrations of DOC that were measured within the soil seepage water were not found to be representative of the DOC concentration of the soil as a whole.

4) Surface Flow

The flow that occurs over the surface of the land has been hypothesised to occur via two flowpaths. The first is Hortonion overland flow where during a rainfall event the water either infiltrates into the soil contributing to the groundwater, or if the precipitation falls at a rate greater than the soils infiltration capacity, there will be an excess of precipitation which will flow over the ground as overland flow. This model is most applicable to areas where there is little vegetation such as in semi-arid and arid climates, but can also occur when the ground is frozen (Ward and Robinson, 1990). This hydrological pathway was observed to be occurring at the Mer Bleue Bog in Canada

(Table 2). This site is characterised by several raised peat domes and had a high yearly export of DOC (8.3 g C m^{-2} yr^{-1}), with export of DOC limited by a low annual runoff (222mm) (Fraser *et al*., 2001). Within the catchment, the highest runoff was measured during the snowmelt during the spring; however the highest DOC concentrations were measured in the summer. This is because during the periods when the snow was melting, the runoff was occurring as fast flow over the peat surface due to the development of ice at the peat snow interface (Fraser *et al*., 2001). The second model of surface runoff is saturation overland flow which is more commonly observed in humid temperate climates than Hortonion overland flow. This model argues that when precipitation falls on a catchment, however long or intense, it will all infiltrate into the soil surface. The shallow water table areas adjacent to the stream channels and subsequently the lower valley slopes become saturated as the water table rises to the ground surface. The infiltration capacity than becomes zero and any further precipitation that falls will be excess precipitation, thus producing saturated overland flow (Ward and Robinson, 1990). When the overland flow dominates the hydrological movement during a storm event, then the concentration of DOC moved to the water body is reduced, due to the reduced infiltration into and interaction within the soil (Soulsby, 1995; Worrall *et al*., 2002;).

2.3.3.3 The influence of high rainfall events and seasonality on DOC concentrations

It has been found that there is a variety of hydrological flow paths that can move DOC from the soil to a water body, and the concentration moved is dependent on the particular flow path that the water follows. However, it is perhaps significant that the highest concentrations of DOC are removed from the soil during high rainfall events which can account for a substantial amount of the yearly carbon export. Schreiber and Duffy (1982) found that between 33 to 77% TOC (total organic carbon) was transported from the soil to the stream system during high rainfall events in five pine forested catchments. A strong relationship has also been identified between DOC concentrations and the discharge in a range of catchments (Grieve, 1984a; McDowell and Wood, 1984; Worrall *et al*., 2002). Measuring the concentration of DOC moved to water bodies during high rainfall events is therefore essential in any study of DOC fluxes. This also needs to be conducted throughout the year as although high rainfall events do produce a large proportion of the DOC exported, the relationship between precipitation and the concentration of DOC exported also varies throughout the seasons. In the UK, the highest DOC concentrations are observed during the late summer and autumn. During the summer months there is increased production of DOC by the soil biota because of increased temperatures (Cole *et al*., 2002) and the DOC accumulates because of the limited rainfall, so following a long dry spell, if a high rainfall event does occur, high concentrations of DOC are measured (Grieve, 1994) Evapotranspiration may also be high during the summer which will reduce runoff and DOC export (Fraser *et al*., 2001). When precipitation begins to increase, in the late summer and autumn, high concentrations of DOC are available for movement from the soil, following an accumulation of DOC throughout the summer months (Grieve, 1984a; Worrall *et al*., 2002). During the winter, although rainfall can be higher and evapotranspiration lower, the concentrations of DOC may become exhausted and are limited by the reduced organic activity and production of DOC during the winter (Grieve, 1984b).

2.3.4 Summary

DOC is a small yet vital component of the global carbon cycle, found in all ecosystems where it is important for the movement of carbon and the formation of organic matter. Yearly exports of DOC, measured in streams, vary considerably between different catchments as seen in Table 2. The concentrations that are measured are influenced by factors including, the catchments' soil carbon store, vegetation, and local climate, principally temperature and precipitation. All these factors contribute to the final concentration of DOC that is measured within the stream system. However, concentrations of DOC have been observed to be increasing within water bodies, the reasons behind these increases are not yet known and this will be further discussed in section 2.4.

2.4 Increasing concentrations of DOC

As discussed in section 2.3, the production of DOC within the soil, and its movement from the soil to the stream system, is a process that is influenced by a number of factors. However, concentrations of dissolved organic carbon (DOC) have increased substantially over the last two decades in North America (Bouchard, 1997; Skjelkvale *et al.*, 2005), the UK (Evans 2005; McCartney 2003; Worrall 2003) and other parts of Europe (Skjelkvale *et al.*, 2005). An example of this trend is shown in Figure 4, illustrating increasing DOC concentrations between 1986 and 2002 within Loch Ard stream 11, one of the site monitored in this study (McCartney *et al.,* 2003).

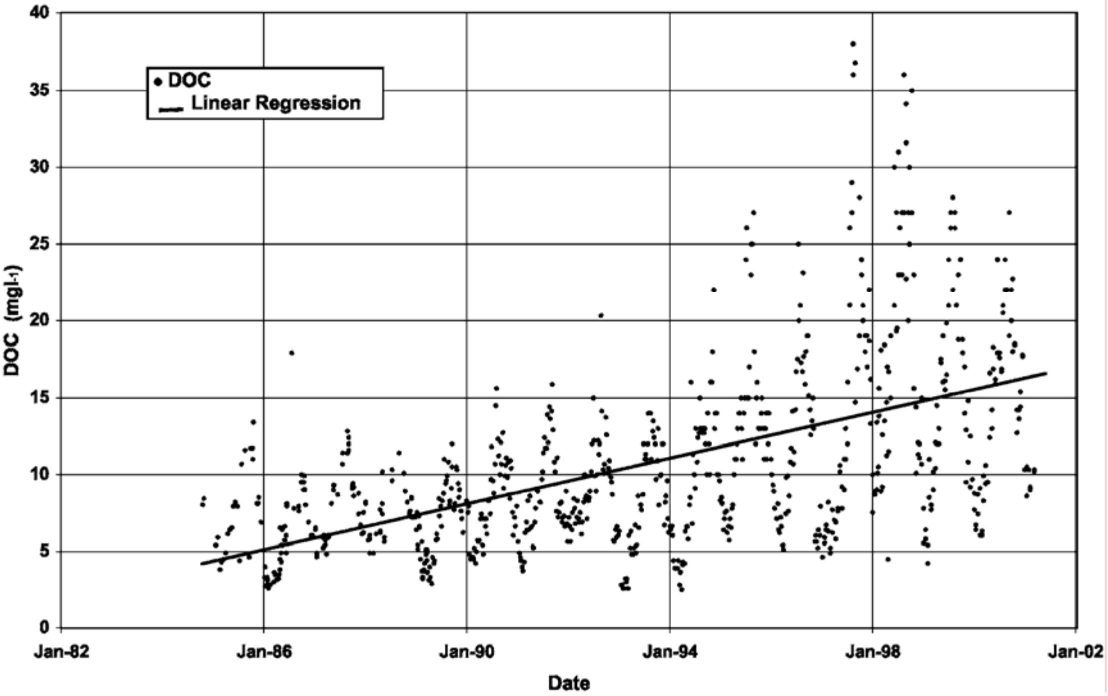


Figure 4: Concentration of DOC over time in Loch Ard stream 11 (McCartney *et al*., 2003)

A similar trend was identified by Evans *et al.* (2005), who measured an average increase in DOC concentration of 91%, over twenty two upland water sites between 1988 and 1993. The most extensive study has been published by Worrall *et al.* (2004), which analysed time series data of DOC concentrations from 198 sites, including 29 lakes, 8 reservoirs and 161 rivers. This analysis identified that 77% of the sites exhibited an upward trend in DOC concentrations, with the remaining sites (23%) showing no significant trend. Perhaps significantly, no sites showed a reduction in DOC concentrations (Worrall *et al*., 2004). There has been much debate about the exact causes of the increase in DOC concentrations that have been observed in water bodies. The principal hypotheses considered to be driving the increases are changes in temperature (Freeman *et al*., 2001), precipitation patterns (Tranvik and Jansson, 2002), and the reduction in soil acidity attributable to decreases in sulphur deposition (Monteith *et al*., 2001). These hypotheses will be examined in the following sections.

2.4.1 Climate change and DOC production

Changes in climate have been identified as one of the potential controlling factors in the globally increasing concentrations of dissolved organic carbon (DOC) measured in water bodies. The influence of climatic variables on DOC concentration has been extensively investigated, with the primary focus on temperature (Freeman *et al*., 2001), and precipitation patterns (Tranvik and Jansson, 2002). This section will describe how the UK climate has changed since the start of the twentieth century, how the climate may change in the future and outline how changes in the climate, specifically increasing temperatures and changing precipitation patterns, which could alter the production and movement of DOC. Other factors linked to climate change, which have been identified to influence DOC exports, including increasing CO_2 concentrations and changes in vegetation community composition and net primary productivity will also be discussed.

2.4.1.1 Climate changes in the UK and Scotland

Global temperature has increased since the beginning of the 20th Century by 0.6°C A corresponding increase has also been observed within the UK and the central England temperature record has measured a near 1°C increase (Hulme *et al*., 2002). Other changes in the UK climate have also been measured. Over the last 200 years winters have been wetter when compared with summers through the UK and more frequent summer heat waves, fewer frosts and winter cold spells have also been measured (Hulme *et al*., 2002). However, climate changes throughout the UK are not homogenous. Table 3 shows changes in temperature in North, East and West Scotland (Barnett 2006). Between 1961 and 2004, temperatures measured in all Scottish regions throughout all seasons have shown an increase, and the overall annual Scottish average temperature has increased by 1°C. A similar trend was observed within the 1914-2004 temperature data; however this showed a smaller overall annual Scottish average temperature increase of 0.5°C, lower than the 1°C increase identified from the central England temperature record (Hulme *et al*., 2002). Comparison of the 1914-2004 and 1961-2004 Scottish temperature data, suggests that there were greater temperature increases between 1961 and 2004. When the individual Scottish regions are examined it can be observed that the East and West have shown the greatest annual increases of 1.08°C and 1.04°C respectively, and it is in the west of Scotland, that the sites used within this study are located. When examining the recent seasonal changes from the 1961-2004, the greatest temperature increase occurred during the winter (1.22°C) throughout Scotland, and the lowest during autumn (0.66°C). The changing temperatures, within Scotland, have also been observed to have affected the growing season start and end dates. In West Scotland, during the 1960s, the start date of the growing season was the 29th March and the end date was the 20th November; it is now starting more than three weeks earlier and ending just over two weeks later (Barnett *et al*., 2006).

Table 3: Mean temperature changes (°C), 1961 to 2004 and 1914 to 2004, in North, East, West and all Scotland, according to season. Statistically significant trends are shown in **bold** (significant at the 1% level) or *italic* (significant at the 5% level) type (After Barnett (2006))

	1961- 2004				**1914-2004**			
	North Scotland	**East Scotland**	**West Scotland**	**Scotland**	**North Scotland**	**East Scotland**	**West Scotland**	**Scotland**
Spring	*1.03*	**1.23**	**1.20**	**1.14**	*0.59*	**0.83**	*0.66*	*0.69*
Summer	**1.06**	**1.12**	**1.08**	**1.08**	0.50	*0.59*	0.43	0.51
Autumn	*0.64*	*0.68*	*0.66*	*0.66*	0.46	**0.85**	**0.68**	0.64
Winter	1.03	*1.39*	*1.31*	*1.22*	0.02	0.45	0.33	0.24
Annual	**0.92**	**1.08**	**1.04**	**1.00**	*0.37*	**0.66**	**0.51**	**0.50**

Table 4 shows the percentage change in precipitation since the start of the measurement period in North, East and West Scotland. Between 1961 and 2004 precipitation increased by 21.1 %, which is equivalent to 240 mm of rainfall a year (Barnett *et al.*, 2006). In the longer term precipitation record (1914-2004), a smaller increase of 6.2 % was calculated. The different percentage change in precipitation was due to the low inter-annual variation in rainfall during the 1960s and 1970s, followed by an increasingly wet period, which thereby produced greater percentage changes in the short term records (Barnett *et al.*, 2006). When the percentage changes in precipitation during the seasons from the 1961 and 2004 are examined more closely, these large percentage changes can be identified, with the largest increase occurring during the winter in all regions of Scotland, with a 61.3% increase in West Scotland. The 1914 to 2004 data shows smaller percentage increases, with decreases calculated across all regions during the summer and the greatest overall increases calculated during the spring (14.3%), with a significant 22% increase in the West of Scotland.

Table 4: Changes in total precipitation amount (percentage), 1961 to 2004 and 1914 to 2004 in North, East, West and all Scotland, according to season. Statistically significant trends are shown in **bold** (significant at the 1% level) or *italic* (significant at the 5% level) type (After Barnett (2006)).

	1961 -2004				**1914 - 2004**			
	North Scotland	**East Scotland**	**West Scotland**	**Scotland**	**North Scotland**	**East Scotland**	**West Scotland**	**Scotland**
Spring	16.2	9.4	17.3	14.8	13.9	6.1	22.0	14.3
Summer	-7.0	0.2	7.3	-0.6	-12.7	*-18.9*	-7.5	-12.7
Autumn	5.3	22.2	5.9	9.1	13.6	0.7	15.6	11.1
Winter	**68.9**	**36.5**	**61.3**	**58.3**	20.9	-0.8	9.0	11.6
Annual	**21.0**	18.4	**23.3**	**21.1**	9.6	-3.5	9.5	6.2

The days of heavy rain (≥ 10mm) measured during the winter in West Scotland, have shown a significant increase of 8.2 days since 1961 when ~50 days of heavy rain were measured, therefore increasing the frequency of storm events. There has also been a 25% reduction of the numbers of days of frost (air and ground) and the snow season has shortened in all regions and seasons (Barnett *et al.*, 2006).

2.4.1.2 Predicted climate changes in the UK and Scotland

Concern over the recent changes in the UK climate has led to the development of models predicting how the UK climate will change in the future. The most recent climate change scenarios were published by the UK climate impacts programme (UKCIP) produced by the Met Offices Hadley Centre regional model (HadRM3). In the UKCIP02 report, four different climate scenarios were presented, based on four possible future global greenhouse gas emission scenarios which were termed Low, Medium-Low, Medium High or High Emissions (Hulme *et al.*, 2002). The changes in the climate are calculated with respect to the average 1961-1990 climate; some of the changes that are discussed here therefore may already have occurred. The low emissions scenario predicts that annual rates of warming over the UK, per decade, will vary from 0.1° to 0.3°C, and for the high emissions scenario from 0.3° to 0.5°C, which would see a warming of 3.5°C by 2080 (Hulme *et al.*, 2002). This temperature change however occurs on a northwest to southeast gradient, with the lowest warming in the northwest of Scotland, where for example, predicted winter temperature increases by the 2080s, are the lowest in the UK, and range from 1°C (Low Emissions) to 2°C (High Emissions) (Hulme *et al.*, 2002). Changes in average temperature will also be seasonal with greater warming seen in the summer and autumn than in the winter and spring (Hulme *et al.*, 2002).

Precipitation has also been predicted to change throughout the UK, with winter precipitation increases by the 2080s, ranging from 5 to 15% under the Low Emissions scenario and greater than 30% for some regions under the High Emissions scenario, but in the summer there will be a reduction in precipitation. Through the winter and summer, the greatest percentage change in precipitation will occur in the eastern and southern part of the UK, with the smallest change taking place in northwest Scotland (Hulme *et al.*, 2002). During the spring, precipitation will decrease in inland areas of the UK and in the autumn, it is predicted that there will be a southeast to northwest gradient, with precipitation in the northwest of Scotland increasing in all scenarios, but decreasing in the southeast between 5 and 20%. However, overall there will be little annual change in the annual total precipitation (Hulme *et al.*, 2002). It is also thought likely that the intensity of the rain will increase throughout the winter, with the most extreme changes in the east of Scotland and least in the west (Barnett *et al.*, 2006).

2.4.1.3 Temperature and DOC

The production of dissolved organic carbon (DOC) within soil is directly linked to temperature, and this is well supported by experimental evidence (Andersson *et al.*, 2000; Andersson and Nilsson, 2001; Neff and Hooper, 2002). Soil incubation studies have been used to identify the effect that temperature has on DOC production, Andersson *et al.* (2001) incubated soils at 4°C and 15°C and Neff and Hooper (2002) used incubation temperatures of 10°C and 30°C. In both studies the concentration of DOC produced was much greater at the higher temperature. The production rate of DOC within the soil has been predicted to increase under higher temperatures, and this will occur through several pathways, some of which are inter-related. Increases in temperature will increase the rate of microbial consumption of the soil carbon (Pastor *et al*., 2003). Soil biota including enchytraeids, are also responsive to climate, and warming of the soil will increase their abundance, thus increasing soil DOC concentrations (Cole *et al*., 2002). Soil warming also increases the burrowing activity of soil fauna, promoting oxygen ingress and resulting in increased decomposition rates (Tipping *et al*., 1999). The rate of decomposition by soil biota may be further increased by changes in the position of the water table. Increased temperatures will change the depth that is exposed within the peat profile, allowing further aerobic and/or anaerobic decomposition, along with increased periods of drought (Pastor *et al*., 2003). The DOC that is produced during drought periods will be either stored within the peat, or exported to the atmosphere through microbial respiration (CO_2-C and CH_4-C) (Pastor *et al*., 2003). During drought periods reduced concentrations of DOC are removed from the soil when the soil is re-wetted the carbon becomes re-mobilized and the concentrations of DOC increase (Turunen and Moore, 2003).

Another impact of temperature increases identified by Freeman *et al.* (2001) is the increased activity of the enzyme phenol oxidase which has been observed to be greater when temperatures increase (producing increased aeration of the peatlands). This may have implications for future changes in the concentrations of DOC as the enzyme phenol oxidase has been identified to be a latch on carbon within peat (Freeman *et al*., 2001). The anaerobic conditions found within the peat system prevent the enzyme phenol oxidase from degrading phenolic compounds. The phenolic compounds then accumulate, and subsequently inhibit the activity of hydrolytic enzymes, which decompose the peat. Increased activity of phenol oxidase, therefore results in increased decomposition of the peat by hydrolytic enzymes, leading to an increase in the release of both DOC and CO_2. This study has however been criticized by Tranvik and Jansson (2002), for not accounting for the influence of changing precipitation patterns on the DOC concentrations measured. The importance of this was however debated by Freeman *et al.* (2002), who argued that over the long term, the effects of discharge on DOC concentration will be limited by the supply of DOC.

2.4.2 DOC, precipitation and discharge relationship

Climate change scenarios in Scotland, have predicted both increases in annual precipitation and the intensity of precipitation (Hulme *et al*., 2002). If increases in precipitation occur, then it would be predicted that DOC concentrations would increase, as more precipitation increases stream discharges and the concentration of DOC within stream water have found to be highly correlated with discharge (Grieve, 1984a; McDowell and Wood, 1984; Worrall *et al*., 2002). Greater precipitation intensity will also produce larger storm peaks; therefore, more frequent intense precipitation will result in more high flow events. These changes in precipitation patterns may also affect the acidity of the soil and the receiving water bodies. For example, during high intensity rainfall events, the water flows through the upper soil horizon; this will also increase the acidity of the water as it is in the lower soil horizons, where the adsorption reactions that reduce the acidity of the water occur (Lawlor and Tipping, 2003). Increases in stormy weather will also increase the amount of sea salt movement and deposition on the land, thus increasing the acidity (Monteith *et al.*, 2001). If soil acidity was to increase, the concentrations of DOC measured may be less, as an increase in acidity would reduce the solubility of the DOC as discussed further in section 2.4.4.

2.4.3 Carbon dioxide and DOC relationship

Carbon dioxide (CO_2) concentrations, within the atmosphere, have shown a steady increase since the industrial revolution, prior to which concentrations were estimated to be 280 ±10 ppm for thousands of years. Concentrations of CO_2, in 1999, reached 367 ppm; this increase is due to anthropogenic emissions, primarily from fossil fuel combustion, but also linked to the production of cement and land use changes (Intergovernmental Panel on Climate Change (IPCC), 2001). Experimental evidence has identified, that under elevated CO_2 concentrations, DOC concentrations measured in peatland pore water increased (Kang *et al.*, 2001; Freeman *et al.*, 2004). Kang *et al* (2001) investigated the effects of increased CO_2 concentration, on fen peat biogeochemistry through incubation of peat cores under elevated (700 ppm) and ambient (350 ppm) CO_2 concentrations for four months. At the end of the experiment, it was observed that the peat incubated under elevated CO_2 concentrations had significantly higher plant biomass, and higher pore water DOC concentrations due to increased plant root exudates. Higher emissions of CO_2 and N_2O were also measured, because of the increased carbon availability in the soil from the higher root exudates, increasing respiration by soil micro-organisms and activating the denitrification process (Kang *et al.*, 2001).

A more recent study by Freeman *et al.* (2004) also found a significantly greater release of DOC from three Welsh peatlands cores (bog, fen and riparian peatland) incubated under elevated CO_2 (+235 ppm), when compared to cores incubated under ambient CO_2. However, when the percentage DOC concentration increases were compared between the peatlands, it was identified that the nutritional status of the sites also played an important role in the DOC concentration produced. The nutrient rich fen and peatland site showed a 49% and 61% increased concentration of DOC, while the nutrient poor bog only produced a 14% increase. The nutritional status of the site is important, as decomposition does not directly respond to elevated CO_2 concentrations, but it is affected by nutrient availability. It was hypothesised, that the increased DOC concentrations that were observed were induced primarily by increased net primary productivity (NPP) along with plant root exudation (Freeman *et al.*, 2004). To test the hypothesis that NPP was driving the increased DOC, the peat monoliths were pulse labelled with $^{13}CO_2$ for 5 hours. At the end of the experiment, the most significant finding was that the proportion of DOC in the soil solution derived from recently assimilated CO_2, was ten times greater than the control. This led Freeman *et al* (2004) to suggest that because the DOC release showed such sensitivity to the elevated CO_2, increases in atmospheric CO_2 may be the mechanism responsible for the observed increases in DOC concentrations, rather than warming, increased river discharges, or the reduction in the proportion of annual precipitation during the summer (Freeman *et al.*, 2004).

2.4.4 Soil acidity and DOC

In the UK soil pH has been identified to have decreased over the last 150 years through the examination of soil cores extracted from lakes (Monteith *et al.*, 2001). This increase in acidification is anthropogenically induced, specifically due to the burning of fossil fuels which emit sulphur dioxide and nitrogen oxides resulting in acid deposition. Recent reductions in acidity are seen to correspond to increases in DOC concentrations measured within water bodies (Harriman *et al.*, 2001; Monteith *et al.*, 2001), suggesting a relationship between soil pH and the solubility of DOC (Chapman *et al.*, 2005).

2.4.4.1 Soil acidity

The acidity of the soil is produced by both natural and anthropogenic processes. Within the soil there are numerous processes that produce H^+ ions, thereby altering the soil pH; these include the formation of carbonic acid, processes involved during the accumulation of organic matter, oxidation of nitrogen and sulphur and the uptake of cations by plants (Brady and Weil, 2002). The organic acids that compose DOC are themselves weakly acidic and they contribute to the buffering capacity of water bodies; Hruska *et al.,* (1999) determined that DOC was important in buffering anthropogenic acidification within a pH range of 4.5-5.2. Another input of acidity to the soil is rainwater which is naturally acidic (pH 5.6) as it reacts with atmospheric carbon dioxide to produce a weak carbonic acid (Botkin and Keller, 1997).

These natural inputs into the soil have also been influenced by anthropogenic activity since the mid 19th century, sulphur dioxide and nitrogen oxide species produced through the burning of fossil fuels, hydrochloric acid emitted from coal burning power plants and ammonia from intensive agriculture (Botkin and Keller, 1997) all contribute to observed increases in soil acidity. These pollutants are either deposited directly via dry deposition, or in precipitation in the form of sulphate, nitrate or ammonium (Monteith *et al*., 2001). The movement of sulphur dioxide and nitrogen oxide, is one of international concern, as airborne emissions can travel between countries, for instance in Sweden more than half of its total acid load comes from abroad (Bengtsson *et al*., 1980). The first attempt to tackle this transboundary pollution was through the convention on Long Range Transboundary Air Pollution (1979) by the United Nations Economic Commission for Europe (UNECE). This convention and subsequent protocols set emissions targets for the international community of sulphur dioxide, nitrogen oxides, ammonia and volatile organic components (Ball and McGillivray, 2001), a plethora of laws were established thereafter in the UK, Europe and Internationally. The most recent protocol was that to Abate Acidification, Eutrophication and Ground-level Ozone-A multi-pollutant and multi-effects protocol, signed in Gothenburg, in 1999. The implementation of these agreements resulted in dramatic reductions in emissions of both sulphur dioxide (SO_2) and nitrogen oxides (NO_X) in the UK, falling by 80%, and 40% of their respective peak emissions in 1999 (NEGTAP, 2001). Deposition of sulphur and oxidised nitrogen have also declined since the peak emissions by 50% and 16% respectively (NEGTAP, 2001). The reduction in acidification is vital as impacts of acidification include reductions in soil fertility particularly in sensitive areas, reduction in surface water biodiversity and leaching of metals such as aluminium, lead, mercury and calcium from soil and rocks into water bodies (Botkin and Keller, 1997).

2.4.4.2 Influence of soil acidity on DOC concentrations

The reduction in acidification that has been measured within the UK (NEGTAP, 2001) has been observed to correlate with increased concentrations of DOC measured within water bodies. Evans and Monteith (2001) identified in all but one of twenty two stream and lake study sites that DOC concentrations had increased between 1998 and 2000 and concluded that this was due to either an increase in soil decomposition during the warm summers in the 1990s, or because of decreases in soil acidity (Evans and Monteith, 2001). To identify the influence that the reduction of acidity has had on DOC solubility and the processes involved, Chapman *et al.* (2005) performed a series of experiments in the field and laboratory. In the field experiment, performed at Moor House, Upper Teesdale, measurements of sulphate (SO_4^{2-}), DOC and water table depth were made, and it was identified that the years with the lowest DOC concentrations also had the greatest summer water table draw down and the highest sulphate concentrations in the soil solution. This influence of drought periods, on sulphate concentrations was also recognized by Harriman *et al.* (2001), in a study of 37 streams and lochs in Scotland between 1976 and 2000. They found that during the year 1995, which had a very hot and dry summer, the majority of the water samples subsequently taken had increased sulphate and nitrate (NO_3^-) concentrations which in some cases doubled in streams that had dried up and were subsequently re-wetted (Harriman *et al*., 2001). The laboratory experiments carried out by Chapman *et al.* (2005), also found that it is the fall in the water table which increased concentrations of both SO_4^{2-} and H^+ ions, but reduced concentrations of DOC (Chapman *et al*., 2005). This is because aeration within the soil allows the largely undissociated H_2S (hydrogen sulphide) to be oxidised to dissociated H_2SO_4 (sulphuric acid), therefore increasing concentrations of SO_4^{2-} and H^+ (Adamson *et al*., 2001). However, aeration of the soil did increase production of DOC, as after the soil was re-wetted and SO_4^{2-} and H^+ ion concentrations decreased, DOC concentrations increased. This would indicate that the release of SO_4^{2-} and H^+ ions were reducing the solubility of the DOC (Chapman *et al*., 2005). Indeed it has been identified that when the pH increases, DOC becomes more soluble as the pH dependent negative charge on the humus colloids increases (Andersson *et al*., 2000). An increase in pH also has a positive effect on the amount of biological activity in the soil (Andersson *et al*., 2000). Another indicator of increased soil acidity is increases in concentrations of the cations Na^+, Mg^{2+} and C^{2+} which have been observed to correspond with increases in SO_4^{2-} and H^+ ions (Adamson *et al*., 2001) These cations which are held on humus and clay colloids along with potassium can neutralise soil acidity (Monteith and Evans, 2001) through their exchange with H^+ ions but are subsequently leached from the soil. The exchange complex then becomes increasingly dominated by acid cations (H^+ and Al^{3+}) (Brady and Weil, 2002). However, this buffering by the cations can only continue if the supply of cations is maintained, which they may not be, if the weathering of the bedrock is too slow to maintain the supply of base-cations, or if the site is acid sensitive and base cation generation is slow (Monteith and Evans, 2001), resulting in these acid cations leaching from the soil and acidifying water bodies (Harriman and Morrison, 1982).

Another method of analysing the influence of acidity on DOC concentration is to examine what takes place when the acidity of the soil is reduced through liming. This process involves the addition of lime ($CaCO_3$), either directly to streams or lakes, or to the surrounding soil, where it neutralizes and buffers the acidity (Bengtsson *et al.*, 1980). Liming has for instance been used extensively in Sweden (Svenson *et al.*, 1995), because Sweden has been subject to extensive acidic deposition and its effect on water bodies has been substantial because they are located on low weathering bed rock or surrounded by lime poor soils (Bengtsson *et al.*, 1980). Studies looking at the effects of liming on the production of DOC have identified that increases in DOC corresponded to the reduction in acidity (Andersson *et al.,* 2000), along with reductions in aluminium concentrations (Grieve, 1990b). This is significant as aluminium also plays a role in soil acidity, and is termed an acid cation, as once the Al^{3+} ions are released from the soil by H^+ ions they are both highly toxic to plants and react with water to produce more H^+ ions (Brady and Weil, 2002).

It has been identified that reductions in soil acidity correspond to increases in DOC concentrations, and this relationship could explain why DOC concentrations have been observed to increase over the last two decades during which time acidic deposition has been decreasing. However, this relationship cannot be generalised throughout the UK, as reductions in sulphur deposition have not been homogenous, with greater reductions occurring around the source areas, but little in more remote locations (NEGTAP, 2001). Indeed, Worrall *et al* (2004) found that within 198 lake, reservoir and river sites throughout the UK, DOC concentrations exhibited an upward trend in 77% of the sites. However, because of the time span covered by this research, both acidification and recovery from acidification would be occurring, but no consistent trend in acidification could be matched with the increasing DOC concentrations and some sites within the study also had not be acidified (Worrall *et al*., 2004). Yet, if the reduction in acidity is responsible for the increases in DOC concentrations, than further increases may occur, as the chemical and biological recovery from acidification is not always immediate, and some areas may take a significant time (perhaps decades) to recover (NEGTAP, 2001).

2.5 Implications of changes in DOC concentrations

It has been identified (section 2.4) that a range of factors could account for the increasing concentrations of dissolved organic carbon (DOC) in water bodies during the last few decades. Further increases in DOC concentrations would have several implications, including a reduction in the global carbon store, increase in metal content and the colour of water bodies and associated costs of water treatment.

2.5.1 Reduction in the global carbon store

The peatland carbon store is at particular risk from the effects of climate change. Peatlands hold an estimated one third (455Gt) of the worlds total soil carbon stores (Fraser *et al.*, 2001) and increasing fluxes of DOC from peat catchments, signals increased loss of carbon from these stores. Tundra peatlands are particularly vulnerable to increases in temperature. Temperature increases would induce thawing of peatlands, under both discontinuous and continuous permafrost conditions, thus increasing the active layers and subsequently decomposition (Watson et al., 1998). Increased temperatures would also increase the activity of the enzyme phenol oxidise, which has been theorised to be a latch on carbon in peat (see section 2.4.1), therefore further increasing decomposition (Freeman *et al.*, 2001). Furthermore, it has been identified by Neff and Hooper (2002) that up to 40% of the soil carbon found in peatlands is potentially decomposable over a short time period, and in the artic and boreal environments the decomposition rates are unlikely to be immediately limited. Peat formation would also reduce; an increase in temperature by only 1-2°C accompanied by decreases in soil moisture would lead to a 25% reduction in peat formation in Tundra areas (Watson et al., 1998). This evidence suggests that both a reduction in the global carbon store and an increase in DOC release would occur. However, Bridgham *et al* (1999) investigated the temperature effects on northern peatlands, and have suggested that the northern peatlands have the ability to have a significant degree of internal control over their energy budgets, and suggested that the impacts of an increase in direct heat on the peatlands, may be less easy to predict due to these internal controls. Nevertheless, an understanding of the global carbon stores is essential for predicting the future changes in their storage capacity, as under changing climates storage of carbon within soils will alter (Post *et al.*, 1982). It is particularly important as the carbon cycle has already been detrimentally altered by anthropogenic activity through increased CO_2 production, which will require further sinks. In the UK, it is important for the use in carbon sequestration studies that are relevant to the UK's commitment to the framework Convention on Climate Change (Milne and Brown, 1997).

2.5.2 Water bodies and DOC

Increases in concentrations of dissolved organic carbon (DOC) would detrimentally affect receiving water bodies, changing both their colour and potentially metal concentrations. The movement of metals (Grieve, 1984b; Lawlor and Tipping, 2003; Martinez *et al.*, 2003), and particularly Fe, which also contributes to the colour of the stream (Fenner *et al.*, 2001), have found to be highly correlated with DOC, therefore if DOC concentrations increase, corresponding increases of metal concentrations may be measured. Any increase in concentration of metals within stream water will increase the threat of toxicity to the organisms that live within this ecosystem (Lawlor and Tipping, 2003) and if the water was to be consumed by humans, it would require further water treatment.

2.5.3 Summary

The identification of the causes of global increases in DOC concentrations in water bodies has generated several theories. The principal theory is that changes in climate (temperature and precipitation increases) will increase DOC production within the soil and increase the movement of DOC from the soil to water bodies. Factors associated with climate changes have also been identified to play a role, with both temperature increases and increasing CO_2 concentrations influencing the growth rate of vegetation. This will increase soil carbon stores and along with increased root exudates, produce higher concentrations of DOC which are then available for movement to water bodies. A second theory is that reductions in sulphur deposition have reduced soil acidity, thus increasing the decomposability of DOC. It is however difficult to isolate the reasons behind DOC increases, and they may be inter-related, and it is suggested that further increases in DOC are limited by its supply. It is essential to understand why DOC concentrations are increasing, as future changes in the climate, and changes in soil acidity may further increase concentrations of DOC. This will have a range of implications including a reduction in the global carbon store, increase in water colour and increases in metal content of water bodies.

2.6 Project Aim

The overall aim of the project is to determine if the relationship between Dissolved Organic Carbon (DOC) concentrations and discharge has changed over a 20 year period in small stream catchments in Scotland, in order to better understand the role of hydrology in driving changes in DOC concentration.

2.6.1 Objectives

To achieve the aim of the project a series of objectives must be achieved: -

1. Establish potential controls of dissolved organic carbon concentrations within the three study catchments
2. Model dissolved organic carbon fluxes within the three study catchments
3. Determine if dissolved organic carbon concentrations have changed within the three study catchments since previous research was conducted at the same sites in the early 1980s and 1990s

2.6.2 Hypotheses

The hypotheses that will be tested are:-

- ***Hypothesis 1:*** Temperature and hydrology are the main drivers of short term changes in DOC concentrations in the three streams studied.

- ***Hypothesis 2:*** DOC production has increased due to increases in temperature and/or reductions in acidic deposition since previous research was conducted at the same sites in the early 1980s and 1990s. This results in a change in the slope of the regression between DOC and discharge.

- ***Hypothesis 3:*** The slope of the DOC/discharge regression will show a greater change in the forest catchments than in the moorland catchment. Forested catchments were subject to the greatest loadings of acid deposition prior to the 1980s and therefore the greatest reduction in acidic deposition subsequently.

2.7 Site Selection

Three catchments were selected for monitoring within this study; two forest catchments located near Loch Ard in the Queen Elizabeth Forest Park and a moorland catchment located in the Ochil Hills near Stirling. The catchment locations are shown in Figure 5. The sites were selected because they had all been previously monitored and water samples taken for dissolved organic carbon (DOC) measurement. The Loch Ard sites were previously monitored between 1989 and 1991 (Grieve, 1994) and the Ochil Hills site between 1982 and 1983 (Grieve, 1984a).

Figure 5: Location of Study Sites, ● = Loch Ard and ○ = Ochil Hills (Map based on Ordnance Survey material, © Crown Copyright 2004)

2.7.1 Forest Catchments: Duchray and Elrig

Figure 6 shows the area of the two coniferous forest catchments used in this study, the larger Elrig catchment covers 1.51 km^2 and the Duchray catchment covers 0.84 km^2. Samples were taken at grid references NS 468 987 (Duchray) and NS 469 987 (Elrig). The Duchray catchment is a typical V-shaped valley and has steeper slopes (mean slope angle of 11°), than the Elrig catchment (mean slope angle of 9°) (Tetzlaff *et al.,* 2007). However, the range of altitudes measured in the Elrig (100-280m), is greater than in the Duchray (105-220m) (Grieve 1994). The geology of both the catchments includes slates, grits and schists of the Dalradian series, along with an extensive cover of locally derived morainic drift (Bibby *et al*., 1985). The dominant soil coverage in the Duchray catchment is poorly drained non-calcareous, humic and peaty gleys {Tetzlaff *et al.,* 2007}. However, in the Elrig catchment this soil type covers only 76.6% of the catchment, with a smaller area (21.7%) of poorly drained non-calcareous, gleys and humic gleys, which have a higher permeability and greater depth than the peaty gleys {Tetzlaff *et al.,* 2007}. The Elrig catchment also contains an area of bog (1.7 ha) located in the central section of the stream where the catchment has a flatter floor (Grieve, 1994). The principal vegetation cover within both catchments, as illustrated in Figure 7, is Sitka Spruce, Scots Pine and Lodgepole Pine, and in the Elrig, Western Hemlock.

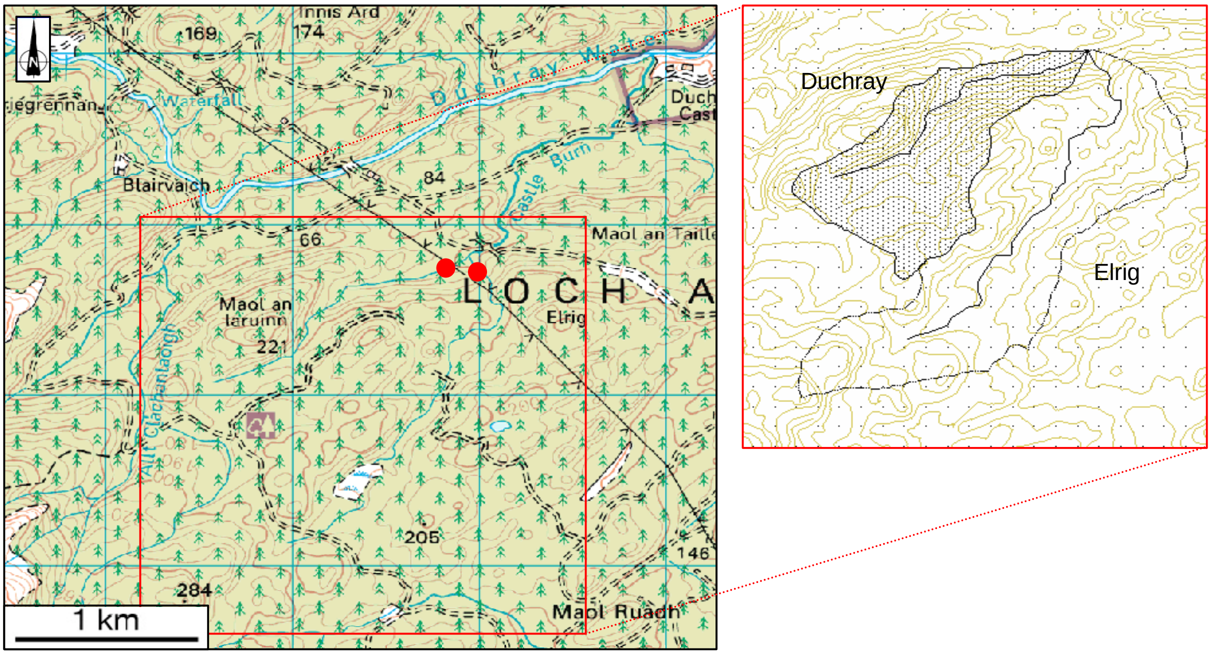


Figure 6: Map showing location of sampling sites at the Duchray and Elrig catchments and the area of the Duchray and Elrig catchments (© Crown Copyright/database right 2006. An Ordnance Survey/EDINA digimap supplied service)

Figure 7: The a) Duchray and b) Elrig streams.

2.7.1.1 Vegetation changes in the Duchray and Elrig catchments

The Duchray and Elrig catchments are located within Forestry Commission land and an active programme of felling is occurring within parts of the catchments. Figure 8 shows the areas of land that have been felled and not replanted, along with forested areas and open land. The majority of the land in both catchments is currently forested; however there is a greater area of open land within the Duchray catchment and the only felled area is also located near the top of the Duchray catchment.

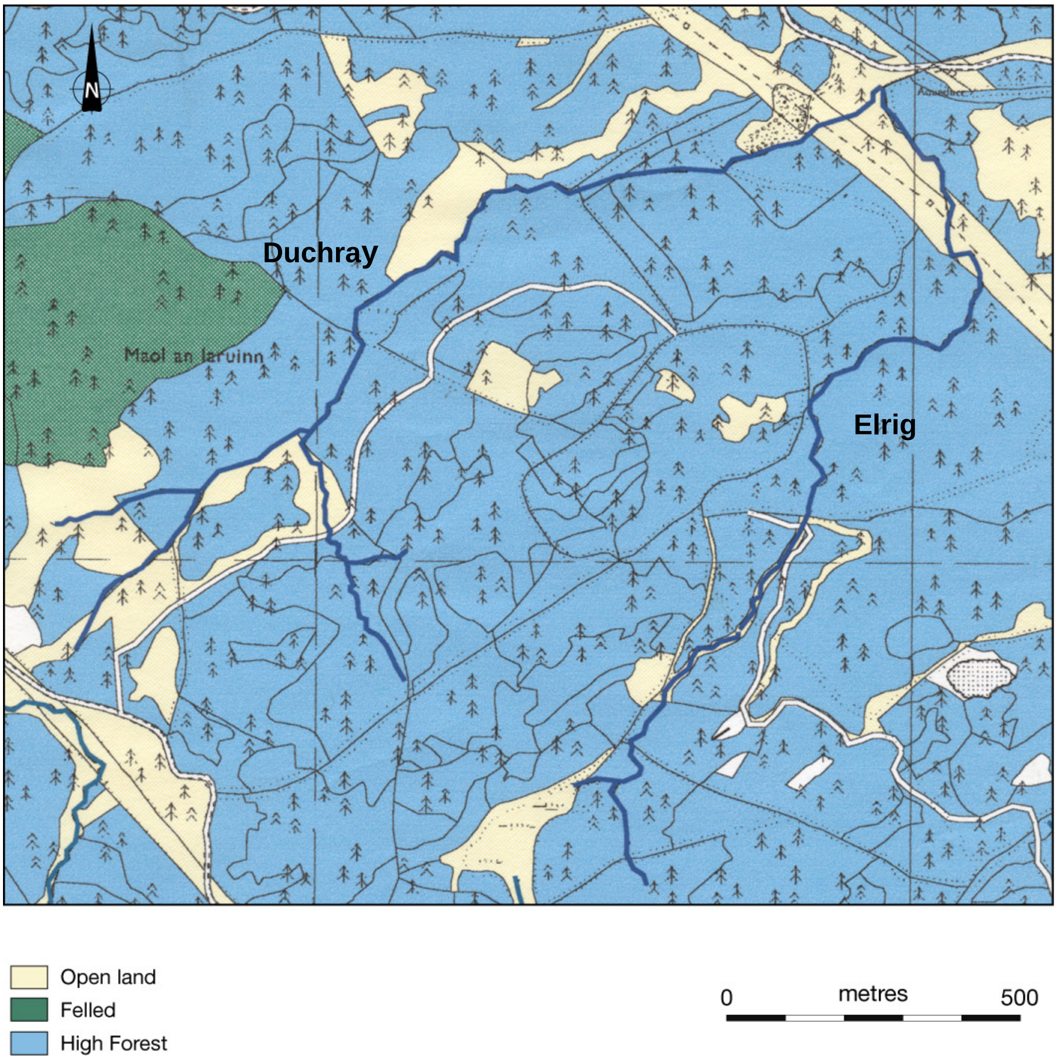


Figure 8: A map showing the felled and forested areas within the Duchray and Elrig catchments (Map based on Ordnance Survey material, © Crown Copyright 2001 and supplied by the Forestry Commission, Scotland).

Figure 9 shows the species of trees planted within the catchments and when they were planted. It can be seen in both catchments that the majority of the trees were planted between 1954 and 1966. Subsequent felling and replanting of trees occurred in both catchments, in the Elrig catchment trees were planted in the east of the catchment in 2000/2001. More extensive felling and replanting occurred in the Duchray catchment, where trees were felled prior to the previous study (Grieve, 1994) and then replanted in 1990, 2000 and 2001. The planned felling within the catchments is also shown in Figure 9, with felling occurring between 2004–2005 at the top of the Elrig catchment when sampling for this study was taking place, and during 2006–2007 after sampling had finished.

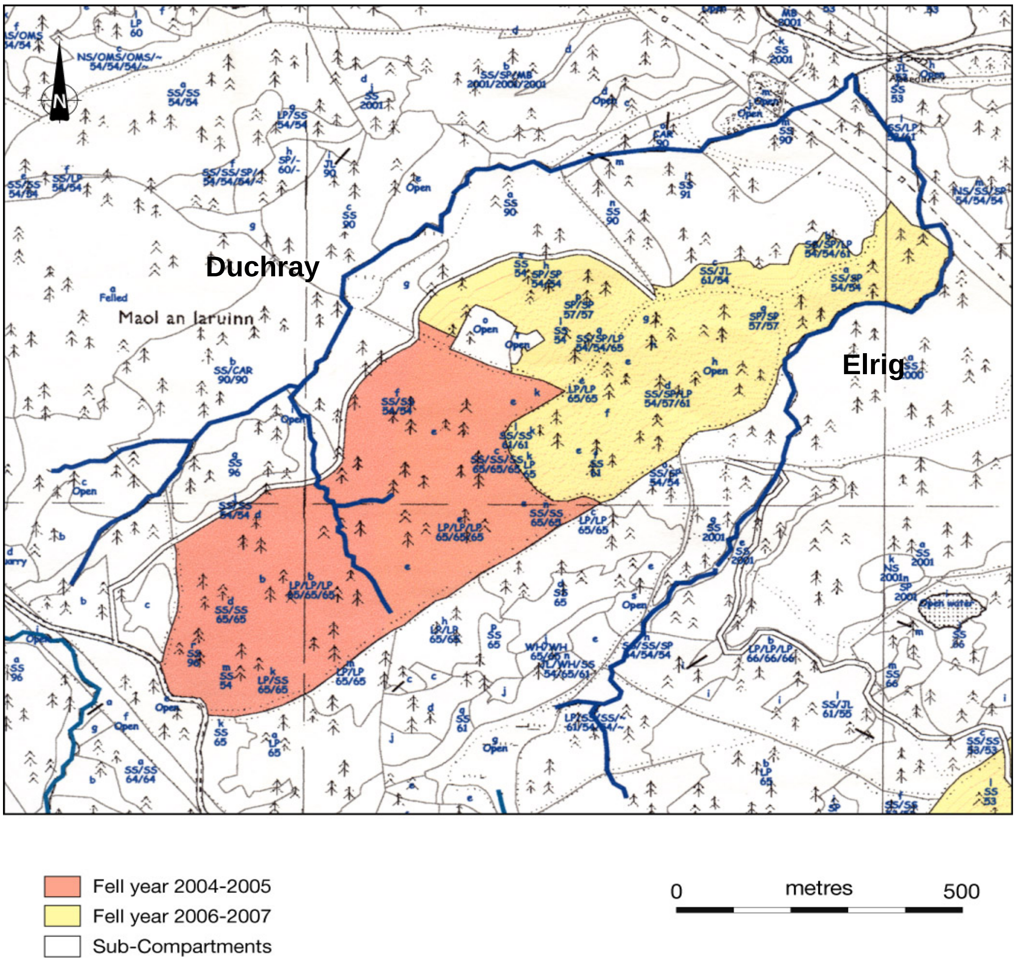


Figure 9: Map showing the species of tree species planted within the Duchray and Elrig catchments, when they were planted and the planned felling of trees, between 2004 and 2007 (Map based on Ordnance Survey material 2001, © Crown Copyright and supplied by the Forestry Commission, Scotland).

2.7.2 Moorland catchment: Ochil Hills

Figure 10 shows the Ochil Hills catchment, a small catchment (0.51 km^2) which drains to the Allan Water. Samples were taken at grid reference (NN 863055). The solid geology of the Ochil Hills catchment is 75% Devonian lavas (andesites and basalts) and 25% Old Red Sandstone with localised patches of boulder clay (Grieve, 1984b). Peat is the dominant soil type in the catchment (75%), freely drained, peaty podzols are found at the top of the catchment, and further down the catchment the stream passes through blanket peat, and then an area of poorly drained peaty gley soil, then through an area of imperfectly drained podzol where the sample site is located, and at the bottom of the catchment are brown forest soils (Glentworth *et al.,* 1968). The dominant vegetation at the grass moorland site include *Deschampsia flexuosa, Deschampsia caespitose* and *Nardus stricta* with localised coverage of *Juncus spp.* and *Calluna vulgaris* (Grieve, 1984b) and is illustrated in Figure 11. The vegetation has remained constant since the previous research (Grieve, 1984a) and there was limited use of the catchment for grazing during the present study.

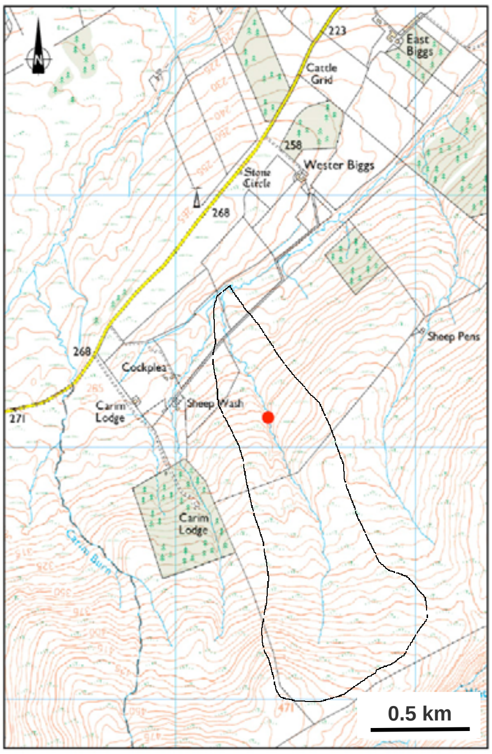


Figure 10: The Ochil Hills catchment (outlined in black) and sampling site (red circle) (© Crown Copyright/database right 2006. An Ordnance Survey/ EDINA digimap supplied service).

Figure 11: The Ochil Hills catchment, pictured looking a) up and b) down stream

Chapter 3 - Methods

Chapter 3 will discuss the methods of sample collection, discharge measurement and meteorological measurements used in each catchment and the laboratory methods used for the analysis of dissolved organic carbon concentrations will be described.

3.1 Water Sample Collection and Storage

Water samples taken for dissolved organic carbon (DOC) analysis, were collected using an ISCO automatic water sampler at all of the study sites. The samplers were started manually and samples were taken every four hours over a four day period and twenty four samples were collected in total. The samples were collected are soon as possible and refrigerated when returned to the laboratory and frozen once filtered. Initially the samplers were triggered using a water level actuator set at a pre-determined height, which would be triggered during storm events and samples taken at hourly intervals over 24 hours. However, when the water level actuator was used the start of the storm event was often missed and the monitoring of DOC concentrations on the rising limb of the storm event is critical. For instance, when the antecedent conditions in the catchment are dry, high DOC concentrations are measured on the rising limb of a storm event (Soulsby, 1995) which may be missed if the water level actuator was used. It was therefore determined that the sampler would be manually set and samples would be taken at 4 hour intervals so a wider range of discharges could potentially be sampled. This approach was also used in the previous studies at the Loch Ard site where samples were taken at 4 (stream 10) or 8 hour (stream 11) intervals (Grieve, 1994) and at the Ochil Hills site samples were taken at 8 hour intervals (Grieve, 1984a).

3.2 Loch Ard Sites – Field Measurements

Discharge and precipitation data for the Loch Ard sites were collected and supplied by the Scottish Environmental Protection Agency (SEPA). Discharge was calculated using 15 minute stage readings. The stage was measured in a stilling well located in the channel side of the flumes in both the Duchray and the Elrig streams. Precipitation was continuously measured (recorded at 15 minute intervals) throughout the study period at a site approximately 9 km South-East of the Loch Ard sites. The closest raingauge to the sites at Duchray Castle was unfortunately malfunctioning throughout the study period; however the alternative gauge that was used captures approximately 90-95% of the rainfall measured at the Duchray raingauge (SEPA, personal communication).

3.3 Ochil Hills - Field Measurements

At the Ochil Hills catchment a range of environmental data were collected. Discharge was continuously measured, as were an array of meteorological measurements including air, water and soil temperatures, precipitation, wind speed and wind direction. The following sections will detail how these measurements were made and how discharge was calculated.

3.3.1 Discharge Measurement

In order to calculate continuous stream discharges, it is necessary to continuously measure the depth of water within the stream. To produce accurate depth measurements, the water flow needs to be constricted, which can be achieved thorough the use of a weir. In the previous study at the Ochil Hills site (Grieve, 1984a) discharge was calculated using water depths recorded on a stage recorder behind a 120° thin plate v-notch weir which could be used to measure discharges up to 500 L s^{-1} (Grieve, 1984a). However, since the previous study was conducted the weir had fallen into disrepair, so it was replaced 10m downstream with a 90° thin plate weir. The 90° thin plate is the most commonly used weir (Rantz, 1982), and was selected because a large volume of water can accumulate behind the weir, therefore any small changes in water level gives a more accurate change in depth, which is particularly important when measuring lower discharges, it is therefore more accurate than other weirs e.g. the rectangular notch weir (Ackers *et al.*, 1978).

This section will discuss how the weir was constructed and maintained, and how depth measurements taken behind the weir were used to calculate continuous discharge within the Ochil Hills stream.

3.3.1.1 Construction and maintenance of the 90° thin plate weir

To ensure accurate discharges (>1%) were measured with the 90° thin plate weir, the criteria set out in the British Standard (BSI, 1981) method of measurement of liquid flow in open channels, in conjunction with other references (Ackers *et al.*, 1978; Dodge, 2001) were followed in both the construction and maintenance of the weir. A summary of these criteria, and whether each was met, is shown in Table 5. A schematic of the weir plate used is shown in Figure 12, as illustrated the weir can measure up to a head height of 54.4 cm, measuring discharges up to 300 L s^{-1}. This a smaller peak discharge than could be measured using the previous weir, but during the previous study only a small number of high flow events reached 500 L s^{-1}, therefore the new weir would be able to measure the majority of the discharges. The 90° thin plate weir from an up and downstream perspective, is shown in Figure 13.

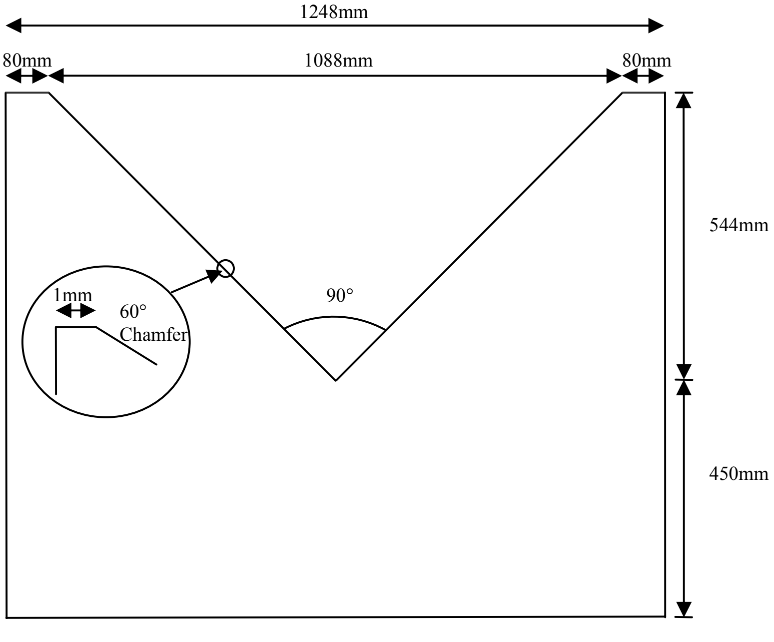


Figure 12: Schematic of V-notch weir plate

Table 5: The criteria to meet in the construction of a thin plate weir (unless otherwise referenced the criterion used are from the British Standard (BSI,1981))

Weir component	Criteria to meet	Achieved
Weir Plate	Constructed of a material that cannot be damaged or distorted	Yes - aluminium sheeting
	The upstream face of the plate to be smooth within a distance of ~ 0.02 m of the crest (Ackers *et al.*, 1978)	Yes
	The surface of the notch should be plane surfaces, forming sharp edges where it intersects with the upstream face of the weir plate	Yes
	The width of the notch surface should be between 1-2 mm, if greater then it should be chamfered on the downstream edges at an angle of no less than 45°. To help prevent water clinging to the downstream face of the weir at low heads than a chamfer of 60° is recommended (Dodge, 2001)	Yes - 60° chamfer
Weir Plate Installation	The plate should be perpendicular to the walls of the channel	Yes
	The weir plate should be water tight where it intersects with the wall and floors of the channel.	Yes
	The centre of the notch should be in the centre of the stream channel	Yes
	The nappe should only touch the upstream faces of weir plate and downstream the channel should be a sufficient vertical distance to ensure free discharge where the discharge is independent of the downstream water level and there must be atmospheric pressure underneath the nappe of the flow over the weir	Yes
Maintenance	The weir plate must be cleaned and silt, vegetation and any obstructions up or downstream of the weir removed.	Yes - continuous maintenance

Figure 13: The Ochil Hills 90° thin plate weir, pictured looking a) upstream and b) downstream

3.3.1.2 Calculation of Discharge

The 90° thin plate weir is defined as a partially contracted weir and as such meets the criteria necessary (BSI, 1981) to use the Kindsvater-Shen formula (equation 3-1) for the calculation of discharge. This calculation can be used to calculate discharges for all triangular notch weirs between 20°and 100° (BSI, 1981).

$$Q = C_e \frac{8}{15} \tan\frac{\theta}{2} \sqrt{2g_n} h_e^{5/2}$$

Equation 3-1

Equation 3-2 was then shortened to equation 3-3.

$$Q = 2.3625 C_e h_e^{5/2}$$

Equation 3-2

Q = the volume rate of flow in cubic metres per second

C_e = the coefficient of discharge

gn = the acceleration due to gravity in metres per second squared (9.8066 m/s^2)

θ = the notch angle i.e. the angle included between the sides of the notch in degrees (90°)

h = the measured head in metres

h_e = the effective head ($he = h + k_h$)

k_h= head correction factor (k_h) (BSI, 1981)

Details of the components used within the Kindsvater-Shen formula, including the coefficient of discharge (C_e), head correction factor (k_h) and the calculation of the measured head (h), are shown below.

a) The coefficient of discharge (C_e)

The coefficient of discharge (C_e) value used for a fully contracted 90° V notch weir is 0.578, however as the weir used in this study is partially contracted, the proximity of the walls and bed of the stream channel may influence the C_e value (Ackers *et al.*, 1978). To take this into account, the value of the co-efficient of discharge (C_e) was taken from Figure 14, which shows C_e values experimentally determined for a range of values of h/P and P/B. The h/P value changes with water depth, and P/B was calculated as 0.2.

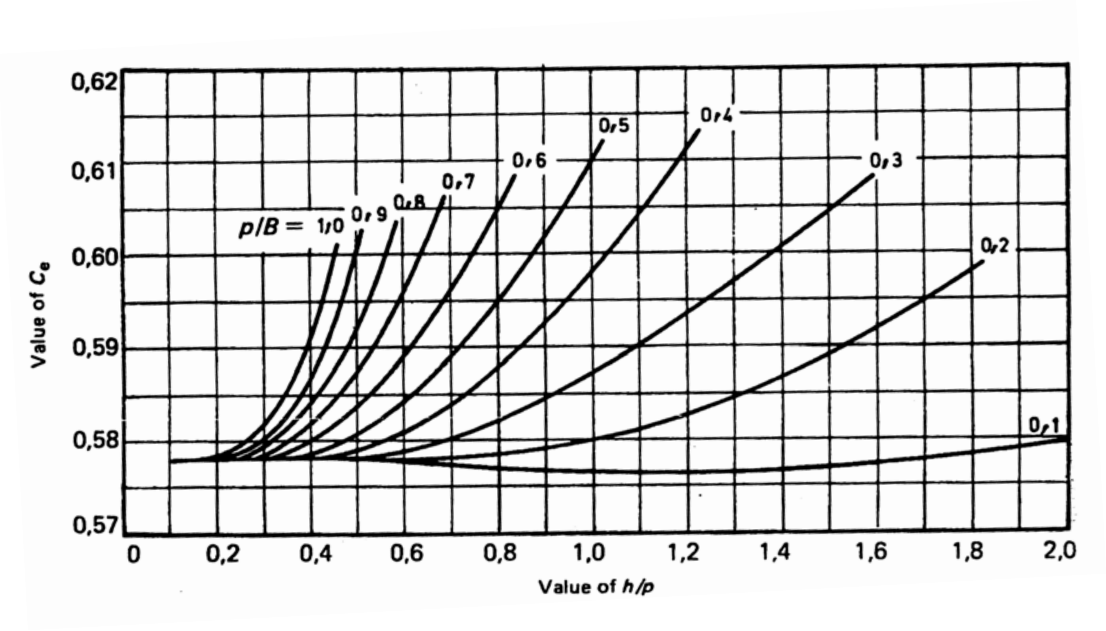


Figure 14: Coefficient of discharge C_e for triangular weirs with a notch angle of 90° (BSI, 1981) (h = Head, P = the height of the vortex with respect to the floor of the approach channel, B = the width of the approach channel)

b) Head correction factor (k_h)

The head correction factor (k_h) is an experimentally determined value, measured in metres, which compensates for the combined effects of viscosity and surface tension (BSI,1981). It is a function of the notch angle and has been found to be a constant value for a corresponding range of h/P and P/B. The k_h value for a 90° thin plate weir notch is 0.00085 m (BSI,1981).

c) Calculation of the measured head

To calculate continuous discharges, it was necessary to continuously measure head; the depth of water above the level of the vortex of the crest of the weir (BSI, 1981). The water depth of the stream was determined using an Intelysis (0-3.5m) pressure transducer, installed at the base of the stream behind the weir plate. The pressure transducer measures a potential voltage (v) which is related to the pressure of the water above it and was recorded on a squirrel data logger at 15 minute intervals. To convert the pressure readings to depth, a series of stream depth (cm) and corresponding pressure readings (v) were noted during the study period, which were used to produce a regression model. An ANOVA was performed on the data which identified that there was a significant increase in stream depth (cm) with increased voltage readings (v) (Depth (cm) = - 1.95 + 147.0 Voltage (v), $F_{1,\ 11}$ = 4169.16 $P < 0.01$). The regression model explained a high percentage of the variation in depth (99.7%); this relationship is shown in Figure 15.

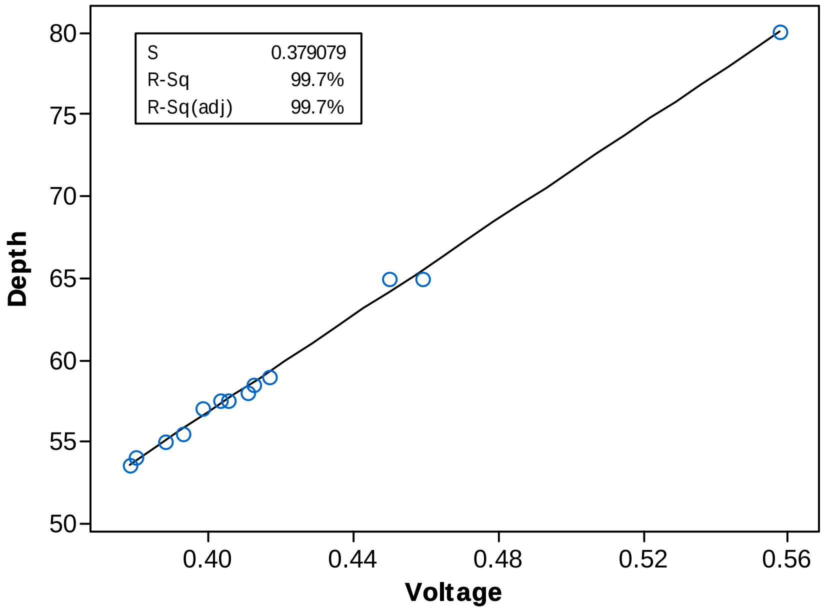


Figure 15: Scatterplot showing the relationship between the depth of water (cm) and voltage (v)

The depth of water within the stream was then calculated using the regression relationship shown in equation 3-3.

$$h = -1.95 + 146.9v$$ **Equation 3-3**

h = the measured head in centimetres

v = voltage

The zero gauge of the weir, the gauge reading corresponding to the level of the vortex of the crest (BSI, 1981) was then established using a Leica TC1010 total survey station which determined the weir notch was 44.4 cm above the pressure transducer. To determine the depth of water above the level of the vortex of the crest of the weir, 44.4 cm was subtracted from all depth measurements. The resulting value is termed h in the Kindsvater-Shen discharge formula.

To test the accuracy of the stage/voltage relationship, an independent calibration was performed where a second stage/voltage relationship was produced. This was achieved by moving the pressure transducer up and down within the stream, taking voltage readings at a series of depths. Discharge was then calculated using both relationships, and a paired t-test comparing a range of calculated discharges (paired t-test: t=1.81, df=11, P=0.095) identified that there is no statistical evidence to suggest that the discharges calculated are different; the independent calibration therefore supports the use of equation 3-3, to calculate depth within the stream.

3.3.1.3 Stage - discharge rating curve

Using the Kindsvater-Shen formula the continuous discharges were then calculated and a discharge depth rating curve was produced. Discharge can then be calculated from height using equation 3-4.

$$Q = 0.0136h^{2.5}$$ **Equation 3-4**

Q = the volume rate of flow in litres per second

h = the measured head in centimetres

The relationship between discharge and depth is plotted in Figure 16, and as the measurements taken to produce the stage/discharge relationship did not cover all discharges potentially occurring within the stream, higher discharges were extrapolated. Therefore errors may occur in the calculation of higher discharges, however a strong statistical linear relationship (99.7%) was found between depth and voltage and few discharges were measured in this region.

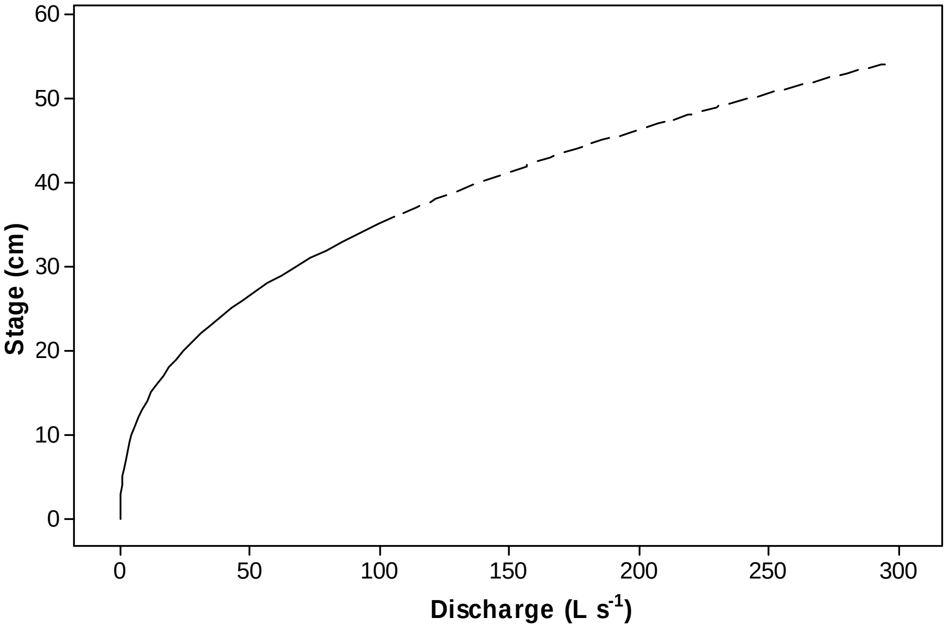


Figure 16: The stage - discharge rating curve for the Ochil Hills stream. The smooth line was generated by stage measurements taken at the site plotted against discharge; the relationship is then extrapolated as shown by the dashed line.

3.3.1.4 Dilution gauging

To check that that the discharge calculation discussed in section 3.3.1.2, was producing accurate discharges, a calibration check was performed using a separate method of discharge measurement, dilution gauging. Dilution gauging has been found to produce accurate discharge measurements (Herschy, 1995) and has produced comparable discharge measurements with both current metering and weir rating (Hudson and Fraser, 2002).

The gulp injection or integration method of dilution gauging was used where a sodium chloride (NaCl) tracer was added in bulk to the stream, under a constant discharge. NaCl was dissolved in a measured volume of water extracted from the stream and the electrical conductivity of the solution was measured using a HANNA HI 9033 multi range conductivity meter. At a point 20m downstream from where the tracer solution was injected, the background conductivity was measured. The tracer solution was then injected into the stream and conductivity measurements were taken every 10 seconds until the conductivity returned to the background level. The discharge of the stream was then calculated using equation 3.5 (Shaw, 1990).

$$Q = \frac{Vc_1}{\int_{t1}^{t2} (C_2 - C_0)dt}$$

Equation 3-5

Q = the volume rate of flow in cubic metres per second

V = volume of tracer added to the stream in cubic metres

C_1= known concentration (or conductivity) of salt added at a constant discharge.

C_2 = sustained final concentration of salt in a well mixed flow.

C_o = background concentration

dt = time interval (10 seconds)

To determine if the discharge calculated using the dilution gauging was comparable with the discharge calculated by the Kindsvater-Shen formula, six separate dilution gaugings were performed during three different calculated discharges as shown in Table 6. It should be noted that the dilution gaugings do not cover the full range of discharges measured within the catchment which would be unpractical to achieve. It can however be identified that the discharges measured using the dilution gauging, and the discharge calculated using the stage measured at time of dilution gauging within the Kindsvater-Shen formula, are comparable. Any inconsistencies between the two calculated discharges are perhaps due to changes in discharge, between the time the dilution gauging was performed, and the depth of the stream was recorded.

Table 6: Comparison of discharges calculated using the dilution gauging method and the Kindsvater-Shen formula using stage measured at time of dilution gauging.

Salt Dilution	Discharge (L s^{-1}) calculated using dilution gauging method	Discharge (L s^{-1}) calculated using the Kindsvater-Shen formula
1	27.62	26.40
1	30.51	26.40
2	18.27	17.81
2	18.45	17.81
3	9.96	9.35
3	9.88	9.35

3.3.2 Meteorological Measurements

A meteorological station was established at the Ochil Hills site in January 2005 and is shown in Figure 17. The station was equipped to measure a range of variables, selected to both provide a record of the weather within the catchment and for use within the modelling section of this project, to understand the influences behind the production and subsequent movement of DOC. The measurements were recorded by two separate loggers; air, water and soil temperatures were recorded by the squirrel data logger which also logged voltage inputs from the pressure transducer for the calculation of discharge. Air temperature, precipitation, wind speed and wind direction were recorded by the Weather Link 5.5. The equipment was installed directly adjacent to the stream where water samples were taken in an area of open ground where no obstacles were present which could potentially affect the readings (Met Office, 2001).The mode of measurement for each of the parameters measured is detailed in Table 7.

Figure 17: The meteorological equipment installed at the Ochil Hills site: This includes, from left to right, the rain gauge, a Stevenson thermometer screen and an anemometer and wind vane.

Table 7: The meteorological parameters measured, their mode of measurement, and the time interval that the measurement was taken, at the Ochil Hills site.

Parameter Measured	Mode of Measurement	Time Interval
Water Temperature (°C)	A thermistor was used to measure water temperature and was secured within the stream.	15 minutes
Soil Temperatures (°C)	Two thermistors were buried at 10cm and 30cm below the soil surface adjacent to the stream where water samples were taken.	15 minutes
Wet and Dry Bulb temperatures (°C)	A Stevenson screen (Plate 1) was constructed next to the sampling site, in which, thermistors to measure wet and dry temperatures were secured.	15 minutes
	A second air temperature sensor connected to the Weather Link 5.5 was placed within the Stevenson screen	30 minutes
Precipitation (mm)	A tipping-bucket rain gauge (Plate 2) was installed to measure precipitation, with a resolution of 0.2mm. To calculate the rainfall that occurred during the interval, the Weather Link 5.5 compared the current total rain value with the previous total rain entry in the archive memory.	30 minutes
Wind Speed (ms^{-1})	A cup anemometer (Plate 2) was installed to measure wind speed. The wind speed was sampled a number of times during the sampling interval by the Weather Link 5.5, these measurements were then averaged and the average wind speed was recorded.	30 minutes
Wind Direction	A wind vane (Plate 2) was installed to measure wind direction. The wind direction reading was sampled a number of times during the interval, to produce the final reading.	30 minutes

3.4 Laboratory Analysis

The water samples, collected from both the Loch Ard and Ochil Hills sites were analysed for their dissolved organic carbon (DOC) concentrations using a Shimadzu Total Organic Carbon (TOC) analyser. Samples from the Ochil Hills site were also analysed for their DOC concentrations using potassium dichromate oxidation. The techniques used to analyse the samples are discussed within this section, and the principles behind the techniques are outlined in Appendix A**.**

3.4.1 Sample preparation for DOC analysis

Prior to dissolved organic carbon analysis, all samples collected from the Loch Ard and Ochil Hills sites, were filtered through Whatman GF/C filters so only the dissolved component remained. This filter was selected to ensure comparability with the previous studies (Grieve, 1984a; Grieve, 1994) which also used GF/C filters. The GF/C filters allow up to 1.2μm organic matter to be filtered through, however, DOC has been generically defined as the fraction of organic matter that passes through a 0.45μm filter (McDonald *et al.*, 2004; Vogel *et al.*, 2000). This definition has not been strictly followed within the literature and was discussed previously in section 2.2.1.

3.4.2 Measurement of DOC concentration

The Shimadzu total organic carbon (TOC) analyser was used to determine the concentrations of total organic carbon (TOC) and total nitrogen (TN) within the samples. Following filtration, samples were poured into glass vials, sealed with parafilm, and placed sequentially into the Shimadzu total organic carbon (TOC) analyser's auto sampler. Prior to and after samples were analysed, a set of standards (diluted on the same day as analysis) and blanks were analysed to ensure accuracy of the results, blanks were also analysed after every ten samples. All Loch Ard samples and the majority of samples from the Ochil Hills site were analysed using the total carbon - total inorganic carbon (TC-IC) method. However, samples from the Ochil Hills catchment which had inorganic carbon concentrations exceeding 10 mg L^{-1} were analysed using the Non-Purgeable Organic Carbon (NPOC) method. The NPOC method was used to reduce the measurement error of the DOC concentration, as when the TC-IC method is used, and high concentrations of both TC and IC are measured, measurement errors of both TC and IC concentrations will increase the final measurement error (Shimadzu Corporation, 2001). Total nitrogen (TN) was measured concurrently with both TOC analysis methods. The principles behind these methods are outlined in Appendix A

3.4.3 Determination of dissolved organic carbon (DOC) by potassium dichromate oxidation

In the previous study at the Ochil Hills site (Grieve, 1984a), DOC was determined by potassium dichromate oxidation. To ensure that the results from the potassium dichromate oxidation method were comparable with the results from the Shimadzu TOC analyser, a sub-set of 70 samples taken at a range of discharges with a range of DOC concentrations (1.74 -12.96 mg L^{-1}) were analysed using both methods. The potassium dichromate oxidation method is described in Appendix A and was adapted from the method of Maciolek (1962) as described in Foster and Grieve (1982) and used in the previous study at the Ochil Hills catchment (Grieve, 1984a).

3.4.4 Comparison between DOC concentrations measured by the potassium dichromate oxidation method and the Shimadzu TOC analyser

When the DOC concentrations measured by the potassium dichromate oxidation method and the corresponding sample analysed by the TOC analyser were compared using a paired t-test, it was identified that there was a significant difference between each DOC concentration measured by the two techniques (paired *t* test; $t = 16.61$, df = 70, $P < 0.05$). Samples analysed using the potassium dichromate method had lower DOC concentrations. The reason behind this difference was perhaps identified by Maciolek (1962), as when investigating the degree of oxidation of a range of organic substances, Maciolek (1962) identified that they were not all oxidised with the same efficiency. The organic substances were split into three groups, each exhibiting, different oxidisability; the carbohydrates were completely oxidised by the dichromate, the lipids were 95-100 % oxidised and the crude proteins were incompletely oxidised (90-95%) (Maciolek, 1962). Maciolek (1962) proposed that the incomplete oxidation could be explained by the formation of acetic acid, which is produced by proteinaceous compounds during decomposition and is difficult to oxidise. Oxidation could be improved through the use of a catalyst such as silver sulphate (Maciolek, 1962).

Although the concentrations of DOC measured using the two different techniques produced significantly different results, an ANOVA was performed on the data and the relationship observed was identified to be significant ($y = 0.901 + 1.18x$, $F_{1,\ 69} = 1120.61$, $P < 0.01$). The regression model explained a high percentage of the variation between the two techniques (94.1%). This strong significant relationship between the two techniques is shown in Figure 18.

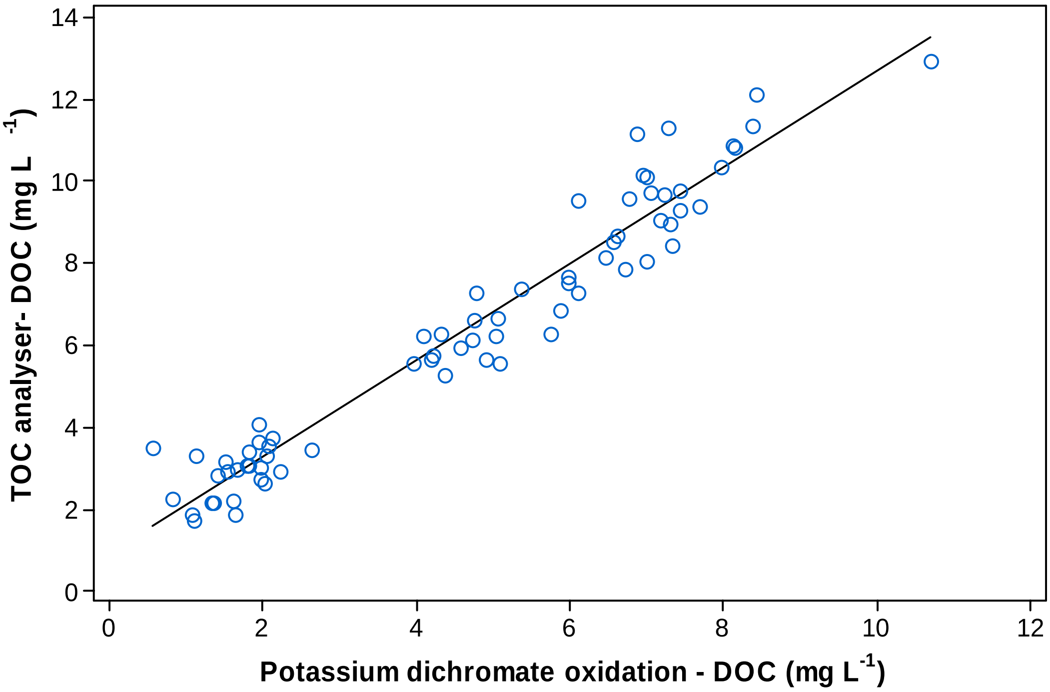


Figure 18: Scatterplot showing the relationship between DOC concentrations measured using the potassium dichromate oxidation method and the Shimadzu TOC analyser.

The strong relationship identified between the two methods, means that the regression equation (Equation 3-6) can be used to convert the DOC concentrations that were measured in the previous study (Grieve, 1984a) into the same concentration range measured in the present study.

$$DOC2005 = 0.901 + 1.18DOC1982$$ **Equation 3-6**

Where:

DOC 1982 = DOC concentrations measured using potassium dichromate oxidation

DOC 2005 = DOC concentration measured using Shimadzu TOC analyser

Chapter 4 - Ochil Hills Catchment

4.1 Introduction

The overall aim of this research project is to identify if dissolved organic carbon (DOC) concentrations have increased in small stream catchments in Scotland over the last 20 years. The aim of this chapter is to establish potential controls of DOC within the Ochil Hills catchment, objective 1 of this thesis and to test hypothesis 1 that temperature and the hydrology of the catchment are the main drivers of short term changes in DOC concentrations in the Ochil Hills catchment. To achieve this it is necessary to further understand the present DOC/discharge relationship in the Ochil Hills catchment. As outlined in Chapter 2, the sources of DOC within a catchment are principally the soil carbon store and vegetation, and the drivers that determine the production rate and movement of carbon are temperature and precipitation. These factors vary extensively between catchments, and their influence on the final concentration of DOC that is measured within the stream system therefore needs to be quantified at the catchment scale. Previous work at the Ochil Hills site (Grieve, 1984a) identified the drivers that were important in influencing DOC concentration within the stream system. These included discharge, rising and falling stage and air temperature. To determine if these drivers are still influencing DOC concentrations and in the same way, the results from a series of sampling events were examined.

4.2 Ochil Hills Sampling

Sampling took place at the Ochil Hills Site from the 16th September 2004 to the 14th February 2006. During this time 22 sample sets were collected, each consisting of 24 samples taken at 4 hour intervals, on an approximate three weekly basis. 470 of these samples were used in the analysis of results. Samples were not taken during May and June, due to the low discharges, when little variation would be seen within the DOC concentration. Sampling frequency was increased throughout the late summer and autumn period when the highest concentrations of DOC were measured.

4.3 Overview of results from the Ochil Hills catchment

Figure 19 gives an overview of the results collected from the Ochil Hills catchment. This shows all precipitation, discharge and dissolved organic carbon (DOC) results collected. It can be seen that a good relationship exists between precipitation and discharge, (precipitation records from the University of Stirling's meteorological station, were used for dates prior to the installation of the Ochil Hills meteorological station in February 2005, and also for other missing data). The boxplots in Figure 19 show the ranges of DOC concentration measured within the Ochil Hills catchment. A limited seasonal trend is observed, with the largest concentrations measured during the summer of September 2004 and August 2005. However, high DOC concentrations were also measured in December 2004 and November 2005 and low concentrations were measured during July and August 2005. This suggests that although season is influencing DOC concentrations, other parameters are also influencing DOC concentrations. To examine the relationship more closely, the overall DOC/discharge relationship was analysed and then the individual seasonal DOC/discharge relationships were investigated.

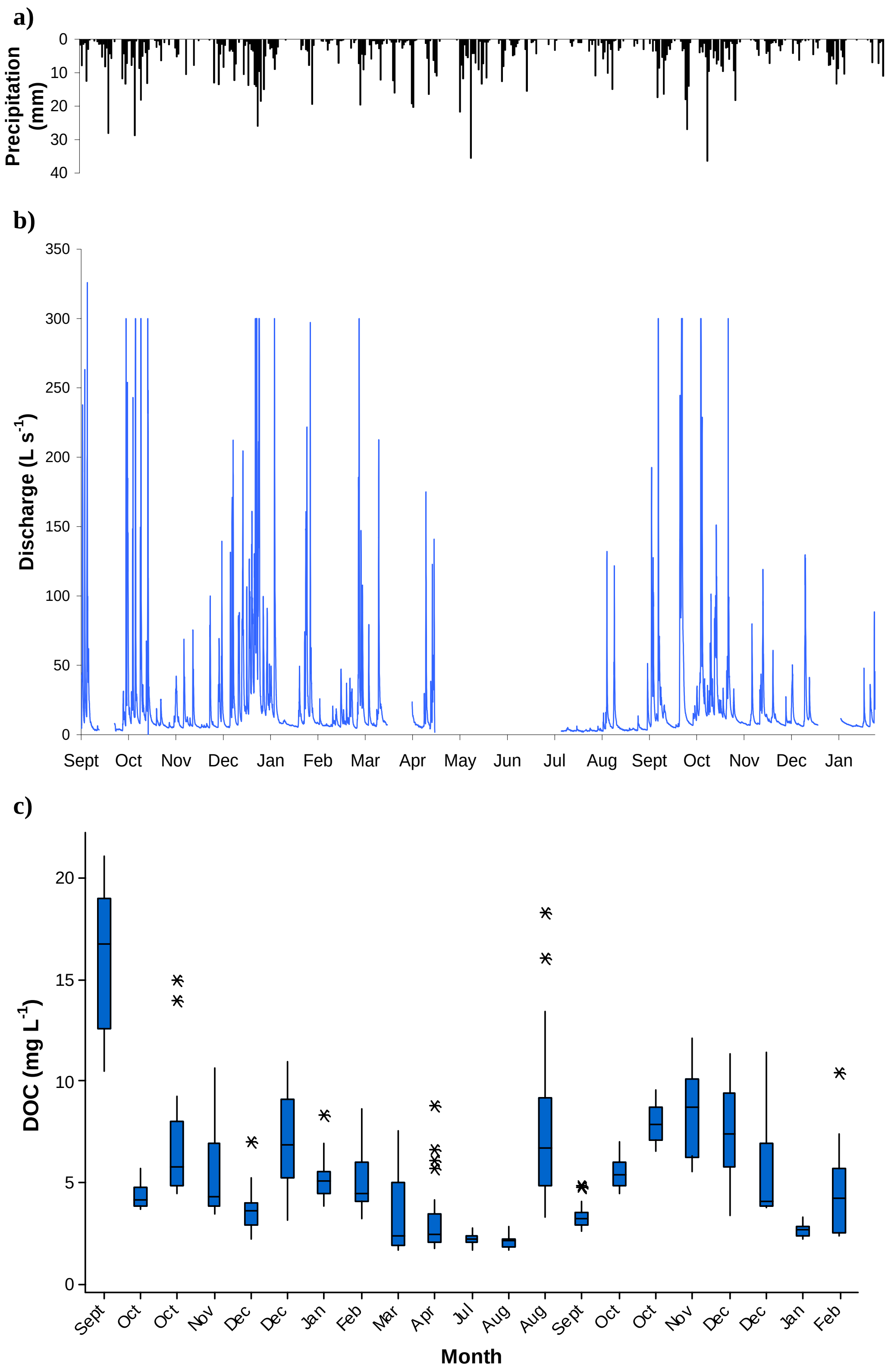


Figure 19: All measurements taken at the Ochil Hills catchment of a) Daily precipitation (mm) (precipitation recorded between the 16th September 2004 and 20th February 2005 and 28th June and 21st September 2005, were measured at the University of Stirlings' meteorological station), b) Average hourly discharge (L s^{-1}) (data missing between the 27th September and 7th October 2005, 3rd and 19th April 2005, 4th May and the 25th July 2005, 8th and 23rd January 2006 and the 18th and 21st February 2006) and c) Boxplots showing 21 sample sets of dissolved organic carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals, between September 2004 and February 2006.

4.4 DOC/discharge relationship

A strong positive correlation has been identified between dissolved organic carbon (DOC) and discharge in a range of catchments (McDowell and Wood, 1984; Worrall *et al.*, 2002). To examine this relationship at the Ochil Hills site, the Pearson's product moment correlation coefficient was calculated, to identify the correlation between DOC concentration and discharge at the time of sampling (all discharges were logged prior to calculation). This showed that a significant positive relationship exists between DOC concentration and discharge within the Ochil Hills catchment (r = 0.765, df = 468, P<0.01), with the two variables having 59% of their variation in common. Figure 20 illustrates this relationship, and shows that DOC concentration does increase with discharge, but at low discharges the relationship is weaker, with little increase in DOC concentration as log Q increases from 0.4–0.8. There is also still some unexplained variance, shown by the considerable scatter around the regression line which may be due to seasonal differences in DOC production.

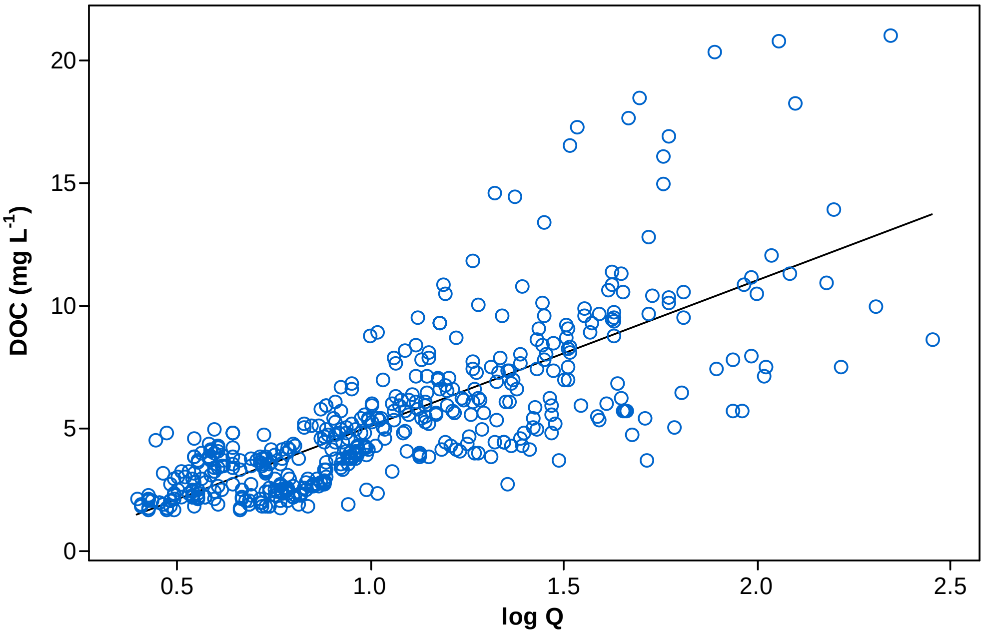


Figure 20: Relationship between dissolved organic carbon (DOC) and the log of discharge (log Q) (R^2=0.59) at the Ochil Hills catchment between the 16th September 2004 and the 14th February 2006.

4.4.1 DOC relationship with low discharge

During periods of low discharge, when limited precipitation fell within the catchment, low concentrations of dissolved organic carbon (DOC) were measured in the stream. This can be observed during three example sampling events in September, July and August 2005 which are shown in Figure 21, 22 and 23. In each event sampled, precipitation was minimal, which resulted in low discharges ranging from 2.36 to 5.23 L s^{-1}, and low DOC concentrations which ranged from 1.68 to 4.88 mg L^{-1}.

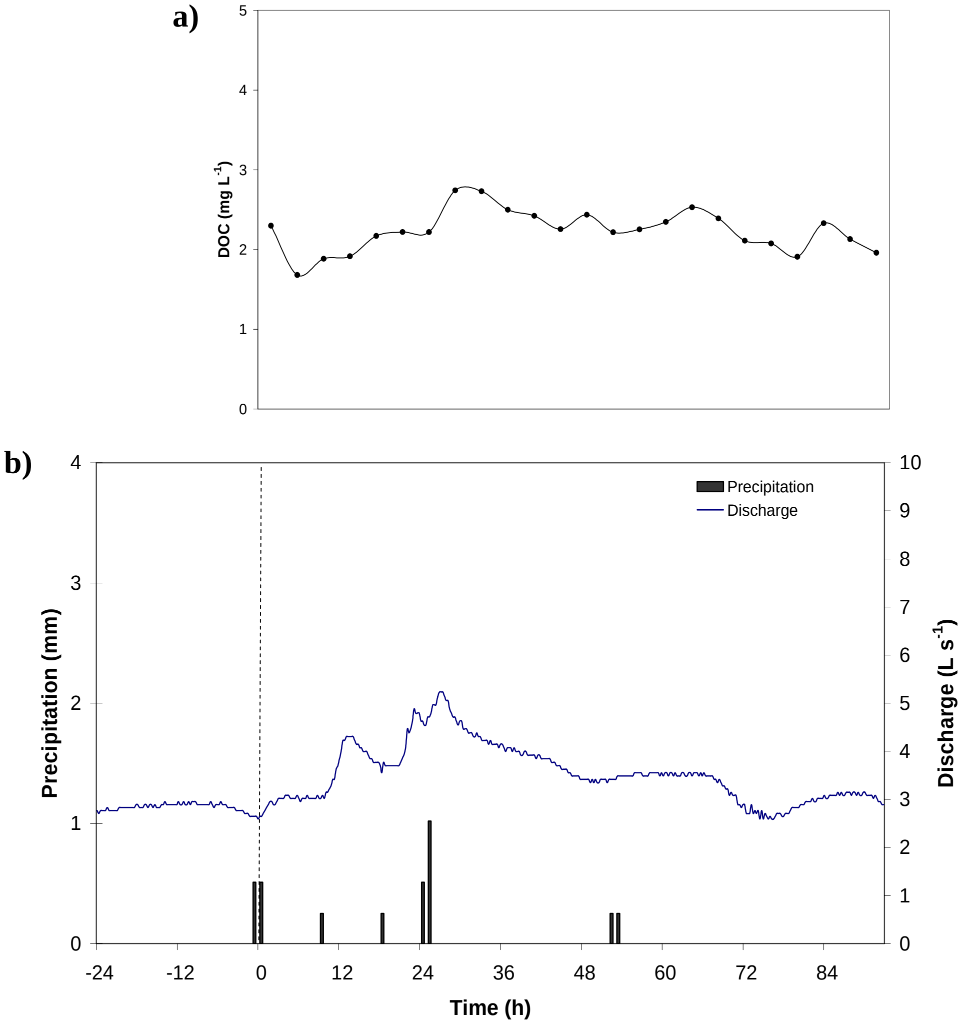


Figure 21: Variations at the Ochil Hills site of a) Dissolved Organic Carbon (DOC) concentrations (mg L^{-1}) taken at 4 hour intervals, between 15.51pm on the 28th July and 11.51am on the 1st August 2005 and b) Discharge (L s^{-1}) and precipitation (mm) taken at 15 minute and 1 hour intervals respectively between 15.51pm on the 27th July and 11.51am on the 1st August 2005. The dashed line illustrates when DOC sampling began.

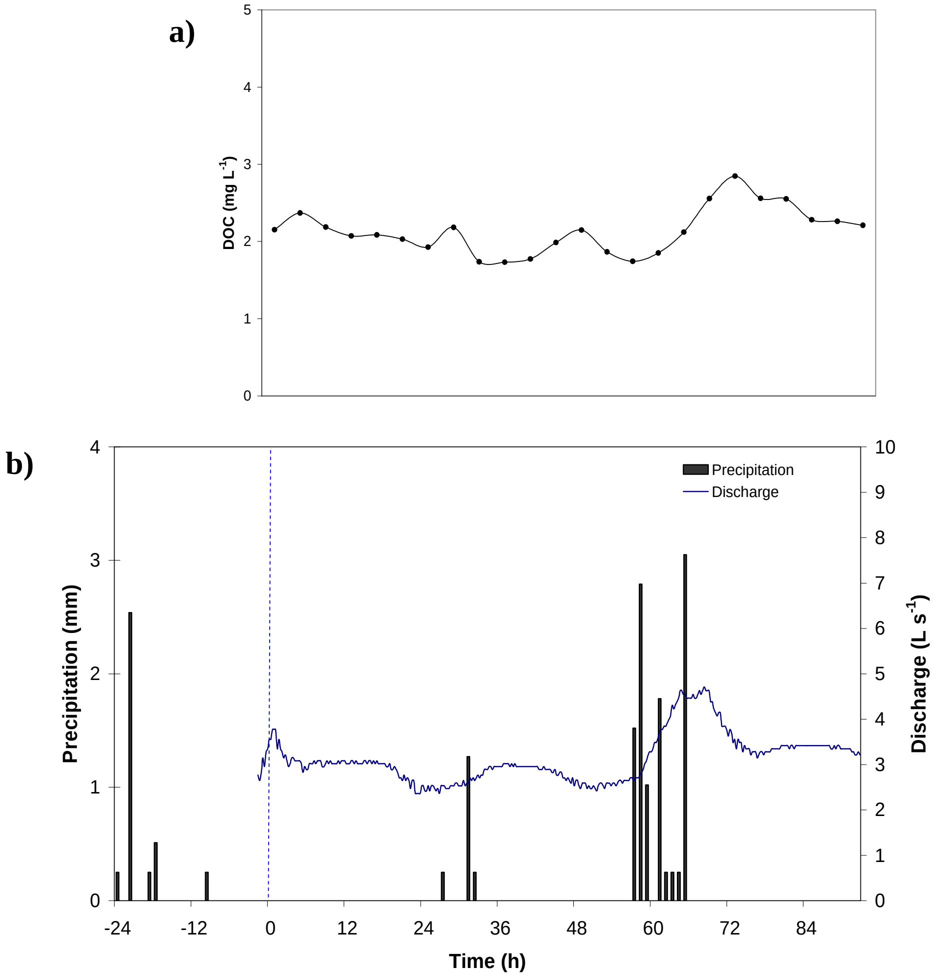


Figure 22: Variations at the Ochil Hills site of a) Dissolved Organic Carbon (DOC) concentrations (mg L^{-1}) taken at 4 hour intervals, between 16.00pm on the 10thAugust and 12.00am on the 14th August 2005 and b) Discharge (L s^{-1}) and precipitation (mm) taken at 15 minute and 1 hour intervals respectively between 16.00pm on the 09th August and 12.00am on the 14th August 2005 (discharge record missing during day prior to sampling). The dashed line illustrates when DOC sampling began.

The low DOC concentrations measured is representative of the source of DOC. When no precipitation falls on the catchment and discharge are low, baseflow is the primary water source of the stream. Concentrations of DOC within the baseflow are typically low, as DOC concentrations are stratified vertically within the soil, with the highest DOC concentrations typically measured within the top horizon, which subsequently reduce with depth, as observed within a podzol and bog by Easthouse *et al.* (1992). This reduction in DOC concentration is due to its metabolization by soil micro-organisms as it moves down through the horizons (Allan, 2001), as well as through sorption processes, as DOC is adsorbed to iron (Fe) in the lower horizons, particularly the mineral B horizon (Moore *et al.*, 1992).

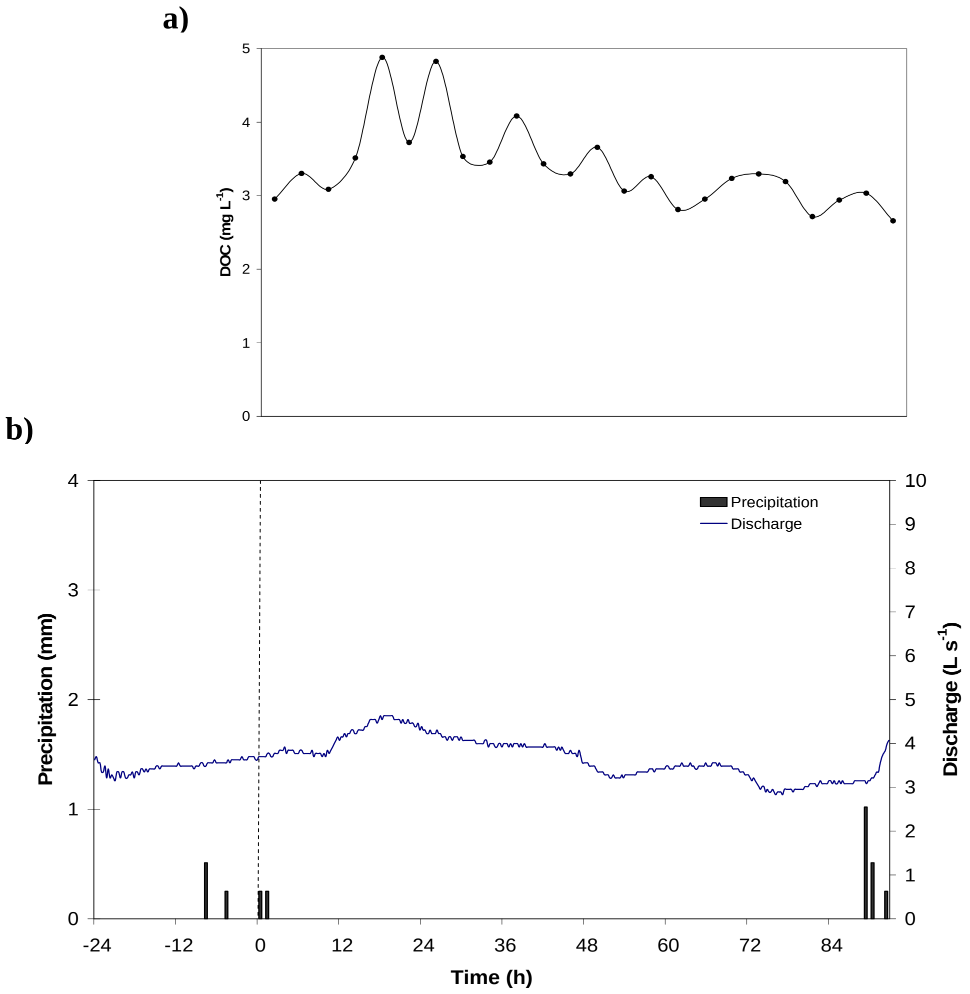


Figure 23: Variations at the Ochil Hills site of a) Dissolved Organic Carbon (DOC) concentrations (mg L^{-1}) taken at 4 hour intervals between 14.00pm on the 9th September and 10.00am on the 13th September 2005 and b) Discharge (L s^{-1}) and precipitation (mm) at 15 minute and 1 hour intervals, between 14.00pm on the 8th September and 10.00am on the 13th September 2005. The dashed line illustrates when DOC sampling began.

The low DOC concentrations measured within the baseflow have also been measured in other upland catchments. Boyer *et al.,* (1997), measured groundwater concentrations of 1.1 mg C L^{-1}, during low flow conditions, however when the water table rose during spring snowmelt, DOC concentrations increased (5.74-8.21 mg C L^{-1}) . Low average groundwater concentrations were also measured by Neal *et al.,* (2005) where the average groundwater concentration was 0.5 mg C l^{-1}, but the average concentrations measured in the streams was 1.5 mg C L^{-1}. The low DOC concentrations measured in groundwater in other studies suggests that the main source of water when no precipitation falls on the catchment is the groundwater. It should also be noted that the time of year that the sample was taken also appears to influence the DOC concentrations, as higher DOC concentration were measured in the September event than in the July or August events. The higher concentrations measured during September 2005, could be explained by the previous antecedent conditions in the catchment, as the first large storm event during the summer of 2005, took place at the end of August 2005, three weeks prior to this event and is shown in Figure 25.

However, although the DOC concentrations measured during periods of low discharge were low, and the strength of the relationship between dissolved organic carbon (DOC) and discharge was reduced (see Figure 20), DOC concentrations within the three sampling events did appear to increase and decrease concurrently with discharge. However, other processes including in-stream processing may be contributing to the DOC concentrations.

4.4.1.1 Dissolved Organic Carbon (DOC) and in-stream processes

It has been identified (4.4.1) that the principal source of the low dissolved organic carbon (DOC) within the Ochil Hills stream during base flow conditions is from the ground water. When the water enters the stream at any discharge, the DOC concentrations that are measured will have been modified by in-stream processing, which can play a significant role in the concentration of DOC that is measured. However, in-stream processes are considered to be less important during high discharges (Mulholland and Hill, 1997). An examination of the role of in-stream processes during low flow conditions will remove the influence that changes in discharge will have on DOC concentrations, so the influence if any that in-stream processes have on DOC concentrations can be identified.

It has been identified that in-stream processes do play a role in DOC concentrations in Scottish peatland streams. Dawson *et al.* (2001a), examined the role of in-stream processing on DOC concentrations, in the Brocky Burn catchment, a small headwater stream in north east Scotland. They measured changing concentrations of DOC along the length of the stream, at the stream's source, concentrations ranged from 1.19 to 6.06 mg L^{-1}, this increased to between 10.0 and 25.3 mg L^{-1} as the stream passed through deep peats, declining to between 7.90 and 19.0 mg L^{-1} at the stream's outlet. This led them to conclude that 11.6 - 17.6% of the DOC had been removed via in-stream processes (Dawson *et al.*, 2001a). Both biotic and abiotic processes are important in the removal and production of DOC within the stream. Biotic processes will be influenced by temperature, and in Dawson *et al.'s* (2001a) study a temperature increase from the source to the outlet was also observed, which may result in increased biotic in-stream processes. Changes in temperature may increase in-stream processing, but it can also change the microbial community structure (Hullar *et al.*, 2006). Few studies have, however, identified a strong relationship between increasing DOC concentration and temperature within streams (Dawson *et al.*, 2001b; Kaplan and Bott, 1982). Diel fluctuations of DOC have been identified by Kaplan and Bott (1982) within White Clay Creek, a stream in Pennsylvania, where the lowest concentrations were measured before dawn; the maximum concentration was reached in the late afternoon, with a subsequent gradual decrease in concentration. The samples were taken during periods of constant discharge (no diel variations) and the explanation for increases in DOC concentrations was excretion from benthic algae which was then modified by bacterial uptake. It was observed that during individual days, concentrations of DOC could increase by up to 20% due to algal excretion, however on an annual basis may account for only 2% of the total DOC exported within the catchment (Kaplan and Bott, 1982). When they analysed the results, they found a positive but non-significant correlation between DOC and temperature and light. Another study by Dawson *et al.* (2001b) measured DOC concentrations every 2 hours over 24 hours in each season, in two acidic peatland streams in north-east Scotland. All but one of the samples was taken at baseflow and they found that no significant diurnal patterns existed in DOC concentrations. However there was no statistical significant difference between day and night time temperatures, therefore diurnal variations may not be expected as DOC decomposition would not be automatically expected.

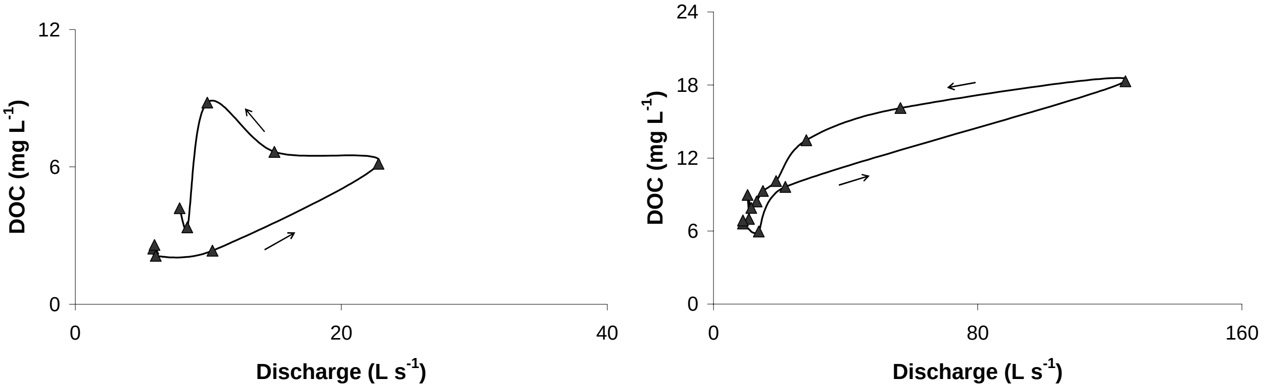
There is little evidence to show that in-stream processing is resulting in substantial changes in DOC concentrations within the Ochil Hills stream, as fluctuations of DOC corresponded to discharge fluxes. This suggests that during periods of base flow, the stream DOC concentrations are primarily influenced by any small changes in groundwater DOC concentrations, with only a small contribution by in-stream processing and any DOC input upstream of the sampling site.

4.4.2 DOC and Storm Events

It has been identified that when no precipitation is falling on the Ochil Hills catchment and discharges are low, dissolved organic carbon (DOC) concentrations within the stream change little. During high flows a stronger relationship between DOC and discharge was observed (Figure 20); however considerable scatter can be observed around the regression line, indicating other DOC controls within the catchment. One possible explanation for this scatter is that during storm events DOC hysteresis is occurring. Earlier research in the Ochil Hills catchment (Grieve 1984a) identified the importance of separating DOC measurements taken on the rising and falling limb of a storm hydrograph for use in modelling DOC concentrations. Determining if hysteresis is occurring and the direction of the hysteresis can in part be used to identify the source of the DOC within the catchment {Evans *et al.,* 1999}, as the type of hysteresis that occurs, is in part governed by the hydrological flowpaths that are followed to the stream, which can be controlled by whether wet or dry antecedent conditions existed within the catchment prior to the storm event (Boissier and Fontvieille, 1995; Bernal *et al*., 2002; Hood *et al*., 2006). The length and intensity of the precipitation can also alter the flow paths that are followed to the stream (Worrall *et al*., 2002). To identify if hysteresis is occurring in the Ochil Hills catchment then DOC concentrations will be plotted against discharge. It has been identified that a minimum of five samples are needed to determine if clockwise or anti-clockwise hysteresis is occurring, as long as samples are taken before and after the storm event at low flow, on the rising and falling limb of the storm hydrograph and at or close to the peak discharge (Evans *et al*., 1999). In addition a selection of storm events will be analysed to identify how hydrological processes within the catchment are controlling the DOC concentrations during storm events.

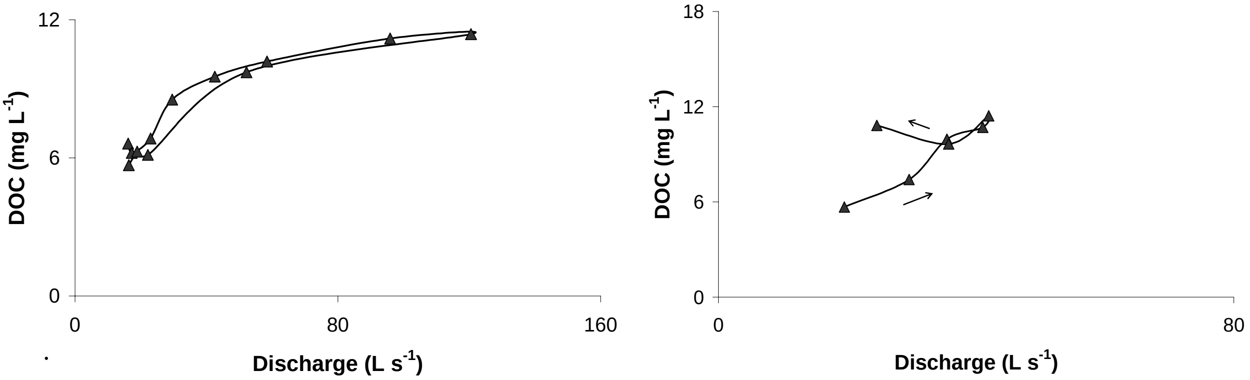
4.4.3 Dry antecedent conditions

Figure 24 shows a series of graphs of dissolved organic carbon (DOC) samples taken during storm events, following dry antecedent concentrations, plotted against discharge. It can be observed in the graphs, that in all the events sampled, except December 2005, where no hysteresis was seen, the DOC concentrations exhibited anti-clockwise hysteresis, where for each value of discharge, the ratio of discharge/DOC on the rising limb is less than the ratio on the falling limb (Williams, 1989). This essentially means that lower DOC concentrations are measured on the rising than the falling limb of the storm hydrograph at similar discharges. It was initially expected that following dry antecedent conditions, the DOC concentration would exhibit clockwise hysteresis (Soulsby, 1995), where the main input sources of DOC are in-stream mobilization and areas adjacent to the stream (Klein, 1984; Bowes *et al.,* 2005). However, the direction of hysteresis has also been associated with the type of catchment, as Bowes *et al.* (2005) identified clockwise hysteresis in a lowland catchment, but anti-clockwise hysteresis in a upland moor site. This suggests that the catchments characteristics can influence the type of hysteresis, as in other upland catchments, anti-clockwise hysteresis has been identified in studies looking at suspended sediment movement (Klein, 1984) and phosphorus movement (Bowes *et al*., 2005). In both these studies it was recognized that it is the source of the sediment/phosphorus which determines if clockwise or anti-clockwise hysteresis occurs. During storm events, the upper slopes of the catchment are a major input source, therefore there is a lag behind the peak of discharge producing anti-clockwise hysteresis. However, hysteresis of DOC has not been observed in all catchments, Evans *et al*. (1999) found no hysteresis occurring, which was perhaps due to the soil type within the catchment, as it was thought that high DOC concentrations would be available in the organic soil, but adsorption in the mineral horizons was depleting the concentrations that were available. Therefore similar DOC concentrations were measured on the rising and falling limb of the hydrograph.



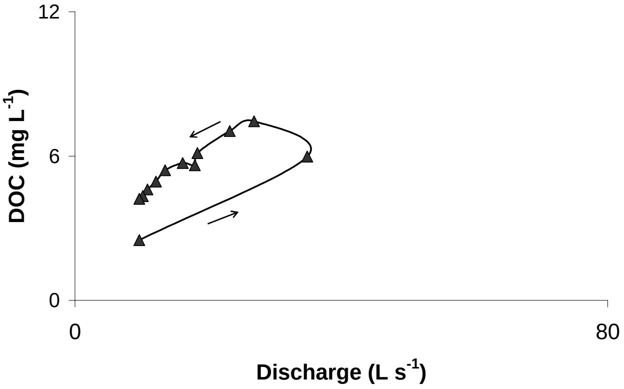
a) April 2005

b) August 2005



c) December 2005

d) December 2005



e) February 2006

Figure 24: Hysteresis loops of dissolved organic carbon (DOC) plotted against discharge, during storm events following dry antecedent conditions in the Ochil Hills catchment.

The anti-clockwise hysteresis that was observed during the majority of storm events following dry antecedent conditions suggests that there is a large store of DOC in the Ochil Hills catchment available for export. The soils within the catchment are highly organic in nature as peat soils dominate (75%), and soils include peaty podzols, blanket peats and peaty gleys. It is therefore suggested that during dry antecedent conditions DOC accumulates within the surrounding catchment and it is not until precipitation falls that the accumulated DOC is exported, the length of time since the previous storm event is therefore potentially an important factor in controlling the concentration of DOC measured within the stream. This can be specifically observed during the August 2005 storm event (Figure 25).

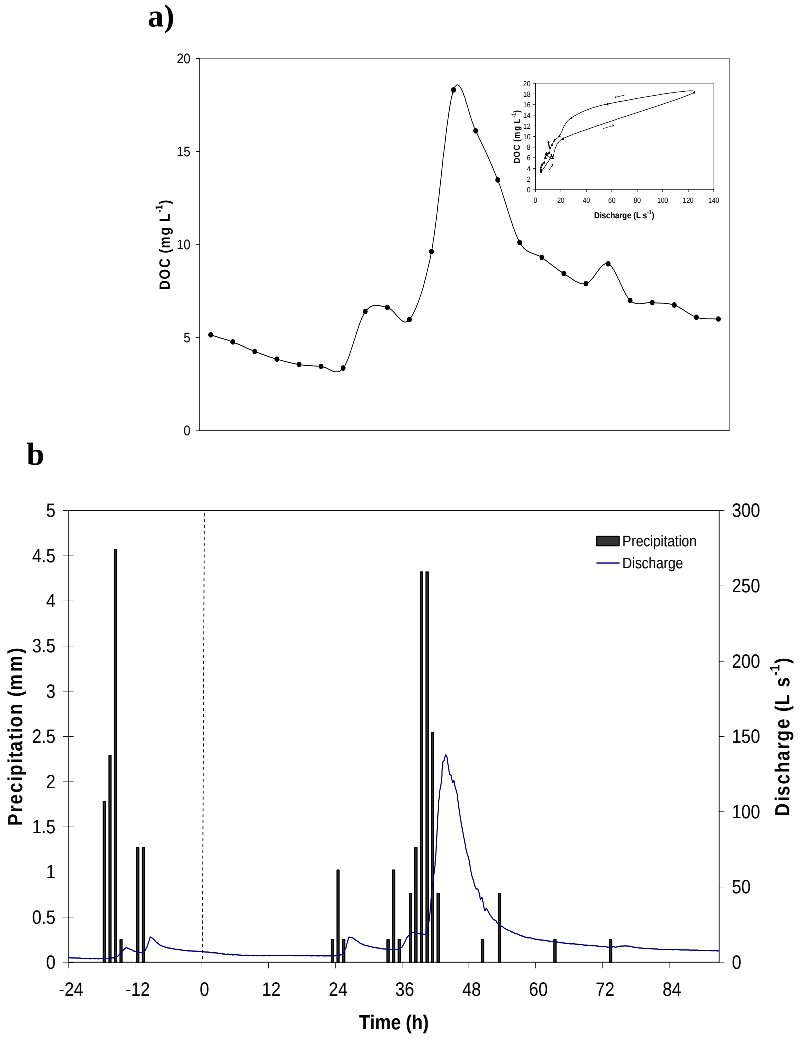


Figure 25: Variations at the Ochil Hills site of a) Dissolved Organic Carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals, between 10.53am on the 22nd August and 06.53am on the 26th August 2005, inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}) and b) Discharge (L s^{-1}) and precipitation (mm) taken at 15 minute and 1 hour intervals between 10.53am on the 23rd August and 06.53am on the 26th August 2005. The dashed line illustrates when DOC sampling began.

This was the first storm event during July and August 2005 as little precipitation fell during July (15mm) and August (32 mm), however the day before sampling, 11.43 mm of precipitation fell on the catchment. The soil was therefore wet the day prior to sampling, which could explain the rapid increase in DOC concentration that was measured during the initial small storm hydrograph, where concentrations increased from 3.36 to 6.40 mg L^{-1}, corresponding to increasing discharges over a 4 hour period from 4.55 to 12.76 L s^{-1}. A further 15.5 mm of precipitation fell on the catchment over a 10 hour period, producing a second storm hydrograph with a peak discharge of 137.65 L s^{-1}, although the peak discharge was not high during this storm event, the peak DOC concentration of 18.3 mg L^{-1} was measured less than an hour after the discharge peak.

The importance of the antecedent conditions, in the release of the available DOC within the soil, is clearly shown by the changing DOC concentrations in the April 2005 event (Figure 26). Antecedent conditions within the catchment were dry, as little precipitation (0.6 mm) had fallen on the catchment during the previous five days, although prior to this, a large precipitation event (~40 mm) occurred. Prior to the precipitation inputs, discharges were low (4.62 - 6.26 L s^{-1}), as were DOC concentrations (1.8 - 3 mg L^{-1}). When precipitation fell on the catchment, DOC concentrations slowly increased with discharge, however the peak concentration (8.8 mg L^{-1}) was not measured until 10 hours following the peak discharge (31.64 L s^{-1}) at a low discharge of 9.93 L s^{-1}. This suggests that when the soil is dry, the time for the soil to become wet will influence the time taken for DOC enriched water to reach the stream. However, during a second hydrograph measured during this sampling event, concentrations were again slow to increase as at a discharge of 44.8 L s^{-1}, the DOC concentration measured 5.7 mg L^{-1}. However, DOC concentrations were not measured on the falling limb of this hydrograph, so concentrations may have again increased, or DOC exhaustion may be occurring.

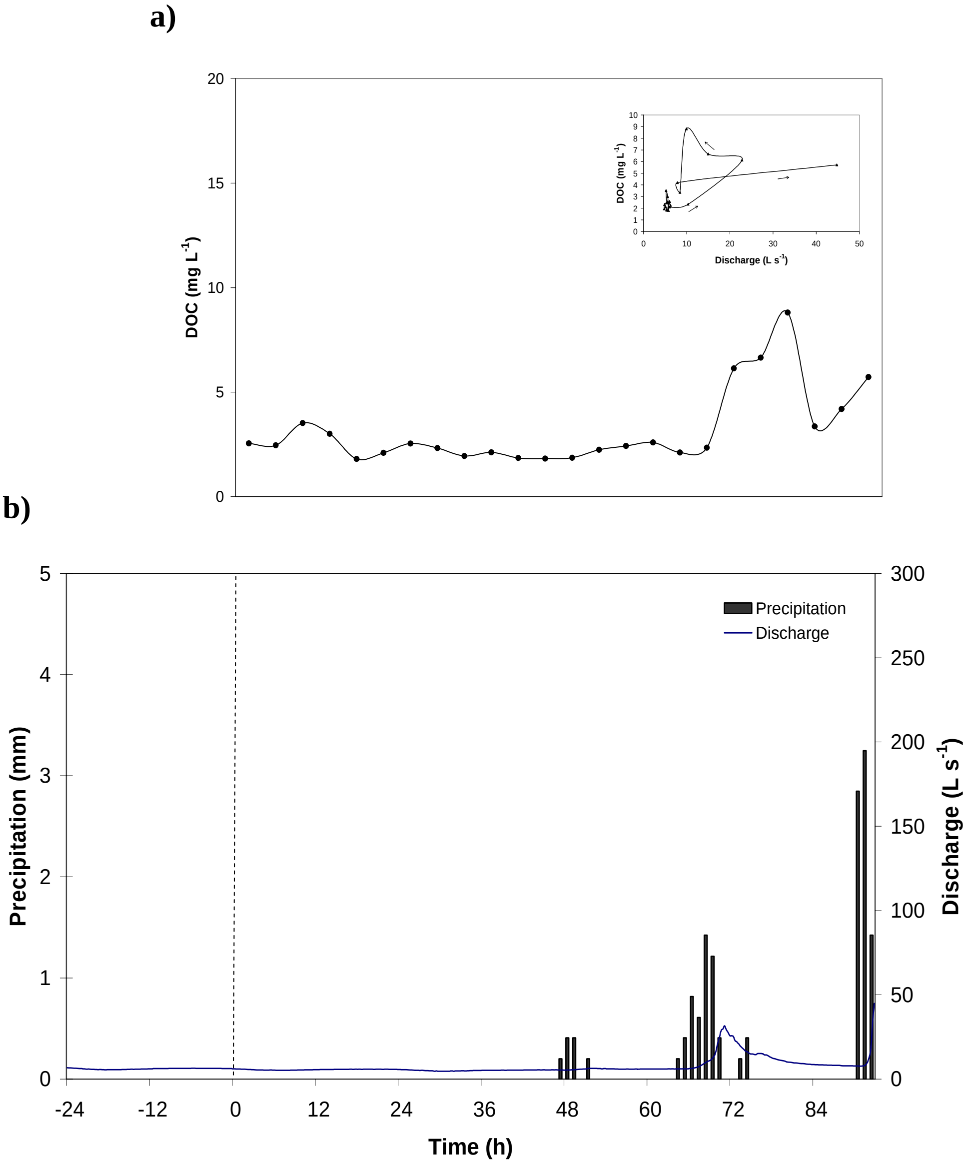


Figure 26: Variations at the Ochil Hills site of a) Dissolved Organic Carbon (DOC) concentrations (mg L^{-1}) taken at 4 hour intervals, between 11.18am on the 24th April and 07.18am on the 28th April 2005, inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}) and b) Discharge (L s^{-1}) and precipitation (mm) taken at 15 minute and 1 hour intervals respectively taken between 11.18am on the 23rd April and 07.18am on the 28th April 2005. The dashed line illustrates when DOC sampling began.

The last two storm events examined show how both the magnitude of the storm event and the length of time of the event can alter the DOC concentration measured. In the December 2005 event (Figure 27) a series of small and one large storm hydrographs were sampled. DOC concentrations within this storm event are initially low as the water is coming from the groundwater. As the precipitation falls on the catchment it is suggested that the soil water from the deeper soils is displaced by the precipitation and is moved to the stream {Evans *et al.*, 1999}. Therefore the initial DOC concentration is low, but increases to 9.81 mg L^{-1}, ~1 hour after the first discharge peak of 44.79 L s^{-1} because the level of the groundwater has increased and the precipitation that is moving through the soil is accessing areas higher in DOC concentration. During the second storm hydrograph, the groundwater may already be high because of precipitation inputs from the previous event and the greater magnitude of the event will further increase the groundwater level. Therefore, new flow paths will be accessed and shallow-sub surface flow may predominate, where DOC concentrations are higher (Evans *et al.*, 1999; Hood *et al.,* 2006) which would account for both the anti-clockwise hysteresis observed and that the peak DOC concentration (11.38 mg L^{-1}) was greater during the second than the first storm hydrograph although at a greater discharge (120.54 L s^{-1}).

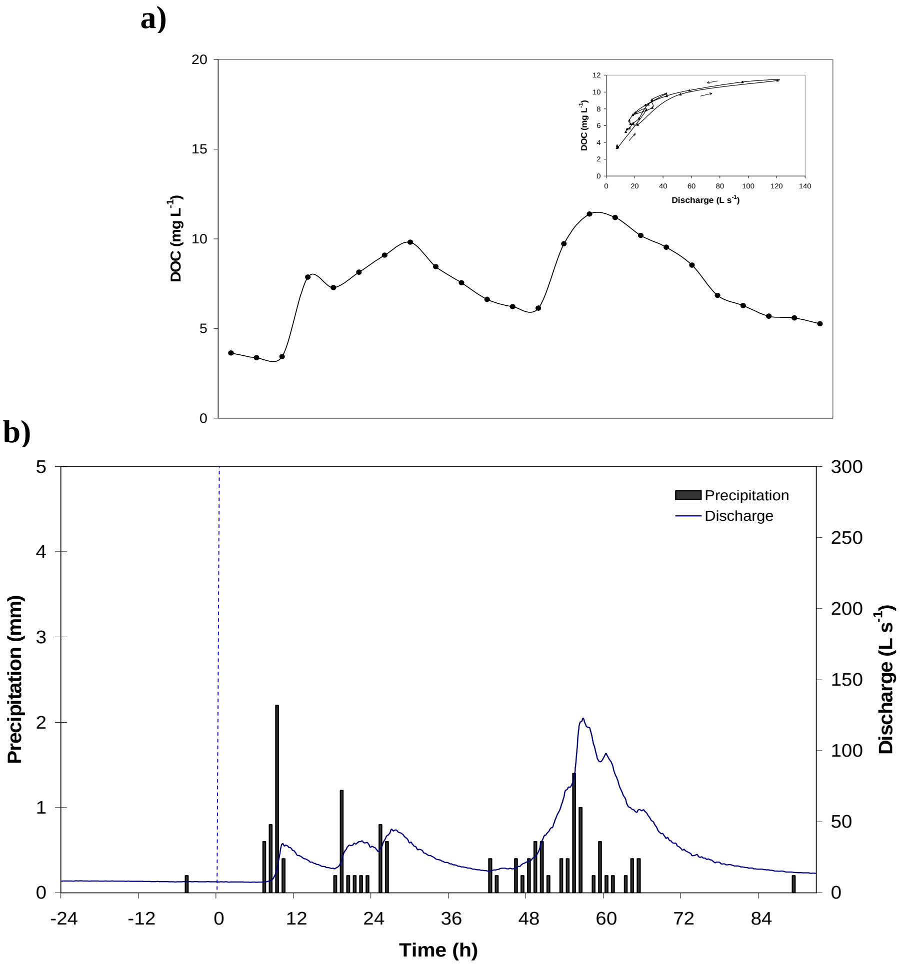


Figure 27: Variations at the Ochil Hills site of a) Dissolved Organic Carbon (DOC) concentrations (mg L^{-1}) taken at 4 hour intervals between 11.40am on the 1st December and 07.40am on the 5th December 2005 inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}) and b) Discharge (L s^{-1}) and precipitation (mm) taken at 15 minute and 1 hour intervals respectively, between 11.40am on the 30th November and 07.40am on the 5th December 2005. The dashed line illustrates when DOC sampling began.

The February 2006 event (Figure 28) further illustrates the importance of the magnitude of the storm event in accessing new dissolved organic carbon (DOC) source areas. Antecedent conditions were dry during the February 2006 event as only 8mm of precipitation fell on the catchment in the week prior to sampling. The start of this sampling period saw stable concentrations of DOC within the stream (2.3 - 2.59 mg L^{-1}). Following the first small precipitation input into the catchment of 7mm falling over an 18 hour period, DOC concentrations measured within the stream did not increase above base flow concentrations until two hours after the discharge peak of 37.74 L s^{-1} when a concentration of 5.98 mg L^{-1} was measured, therefore suggesting that initially the source of the DOC was the soil water, displaced from the soil by the incoming precipitation (Evans *et al.,* 1999). However, during the second larger storm hydrograph event, which peaked at 91.42 L s^{-1}, a much larger increase in DOC concentration was measured increasing from 3.72 mg L^{-1} on the rising limb to 10.45 mg L^{-1} on the falling limb, where samples were taken at similar discharges (51.53 and 53.31 L s^{-1}). This large increase in DOC concentration suggests, that as was observed in the December 2005, the groundwater level has increased further than during the first storm hydrograph, and the flowpath is changing to the highly organic shallow subsurface, therefore accessing much higher concentrations of DOC (Evans *et al.,* 1999; Hood *et al.,* 2006), which is reflected by the increased concentration of DOC measured within the stream.

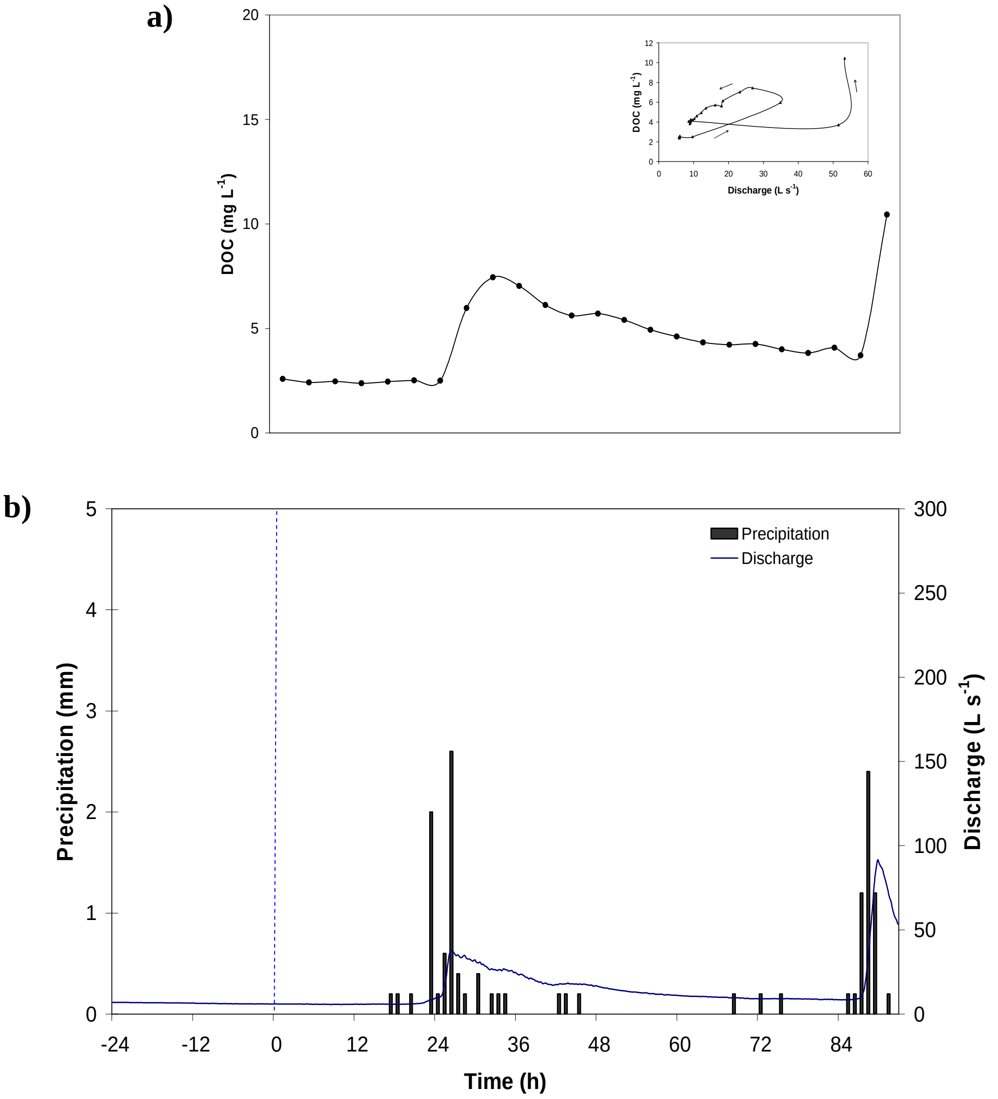


Figure 28: Variations at the Ochil Hills site of a) Dissolved Organic Carbon (DOC) concentrations (mg L^{-1}) taken at 4 hour intervals, between 15.13pm on the 10th February and 11.13am on the 14th February 2006, inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}) and b) Discharge (L s^{-1}) and precipitation (mm) taken at 15 minute and 1 hour intervals respectively, between 15.13pm on the 09th February and 11.13am on the 14th February 2006. The dashed line illustrates when DOC sampling began.

The antecedent conditions within the catchment are therefore integral to the control of the DOC concentration that is measured within the stream, and as was noted within this section, if a second storm event is sampled, then it is this event that shows the most pronounced anti-clockwise hysteresis, which would suggest a large available store of carbon within the catchment and the pre-dominance of the anti-clockwise hysteresis during all the storm events suggests that the DOC concentrations that were measured within the stream are coming from both the immediate catchment and from further within the catchment.

4.4.4 Wet antecedent conditions

Figure 29 shows a series of graphs of dissolved organic carbon (DOC) samples taken during storm events, following wet antecedent concentrations, plotted against discharge. The graphs show that that anti-clockwise hysteresis occurred during all storm events monitored. However, the anti-clockwise hysteresis is more pronounced during November and December 2004, where there is a greater difference in DOC concentration measured on the rising and falling limb of the storm hydrograph. This could be explained by the amount of precipitation that fell prior to the event as larger volumes of precipitation fell prior to the January, February and November 2005 and the plots shows for theses events, that although the DOC concentrations are generally higher on the falling limb than the rising limb, the DOC concentrations are similar during these events.

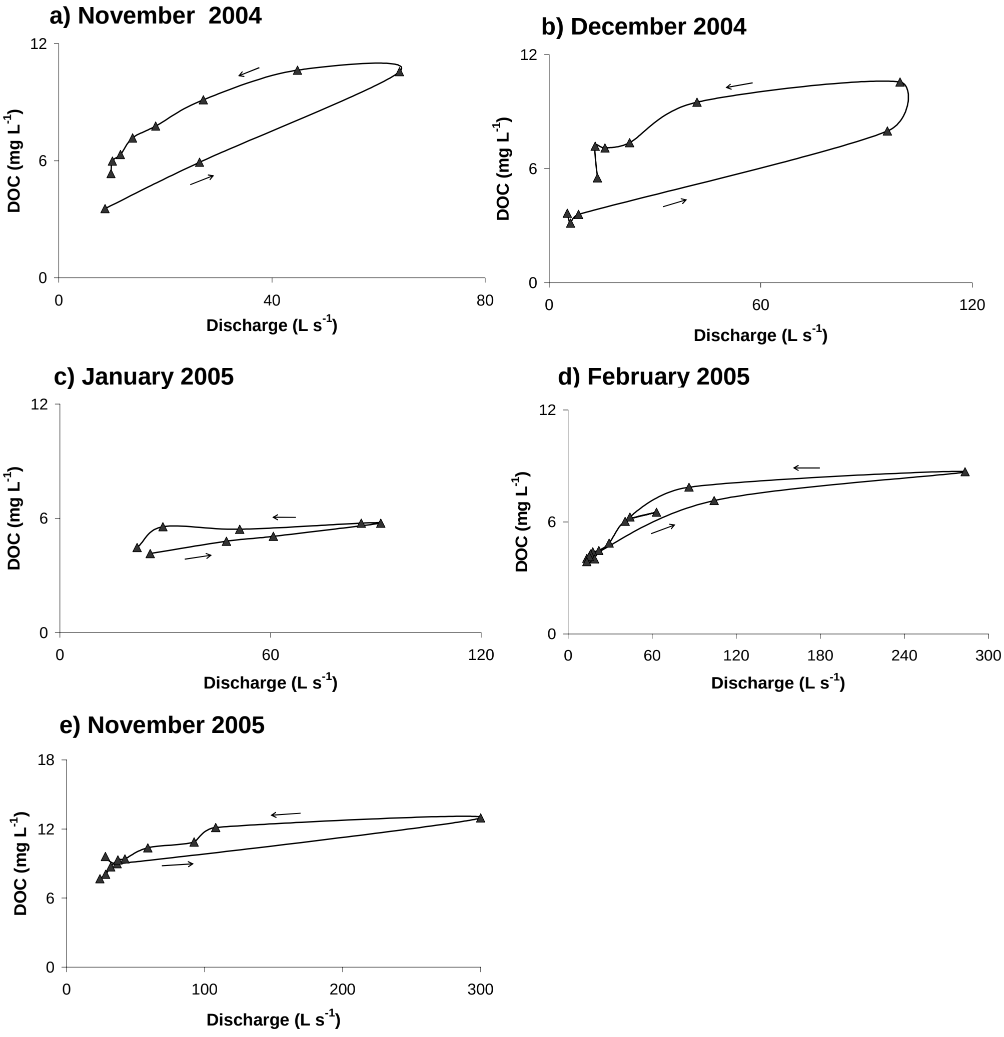


Figure 29: Hysteresis loops of dissolved organic carbon (DOC) plotted against discharge, during storm events following average and wet antecedent conditions in the Ochil Hills catchment.

To determine how DOC concentrations change during storm events that follow wet antecedent conditions, two events during November and February 2005 was examined. In the week prior to the November 2005 event (Figure 30), 30 mm of precipitation fell on the catchment, and a further 30 mm fell during the sampling period, during which two small and one large storm hydrograph were measured. At the start of this sampling set, prior to precipitation inputs, the initial baseflow discharges were higher than those measured following a period of dry antecedent conditions and ranged from 11.29 to 12.45 L s^{-1}, as were the DOC concentrations (5.57 - 6.22 mg L^{-1}). When precipitation began to fall on the catchment, large increases in DOC concentrations were measured, anti-clockwise hysteresis can be observed during the large storm hydrograph where a peak of discharge exceeding 300 L s^{-1} was measured, and ~10 minutes later, the peak DOC concentration was measured (12.96 mg L^{-1}). The anti-clockwise hysteresis that was exhibited by the DOC concentration during the large storm hydrograph, suggests that there is a large concentration of DOC available for movement within the catchment (Bowes *et al.,* 2005; Klein, 1984). This is supported by the fact that DOC sample taken on the rising limb of this large storm hydrograph at a discharge of 36.58 L s^{-1} measured 8.98 mg L^{-1}; however the samples taken on the falling limb had greater DOC concentrations which did not fall to a similar concentration (8.71 mg L^{-1}) as the rising limb, until ~1 day after the peak of discharge at a similar discharge (31.9 L s^{-1}).

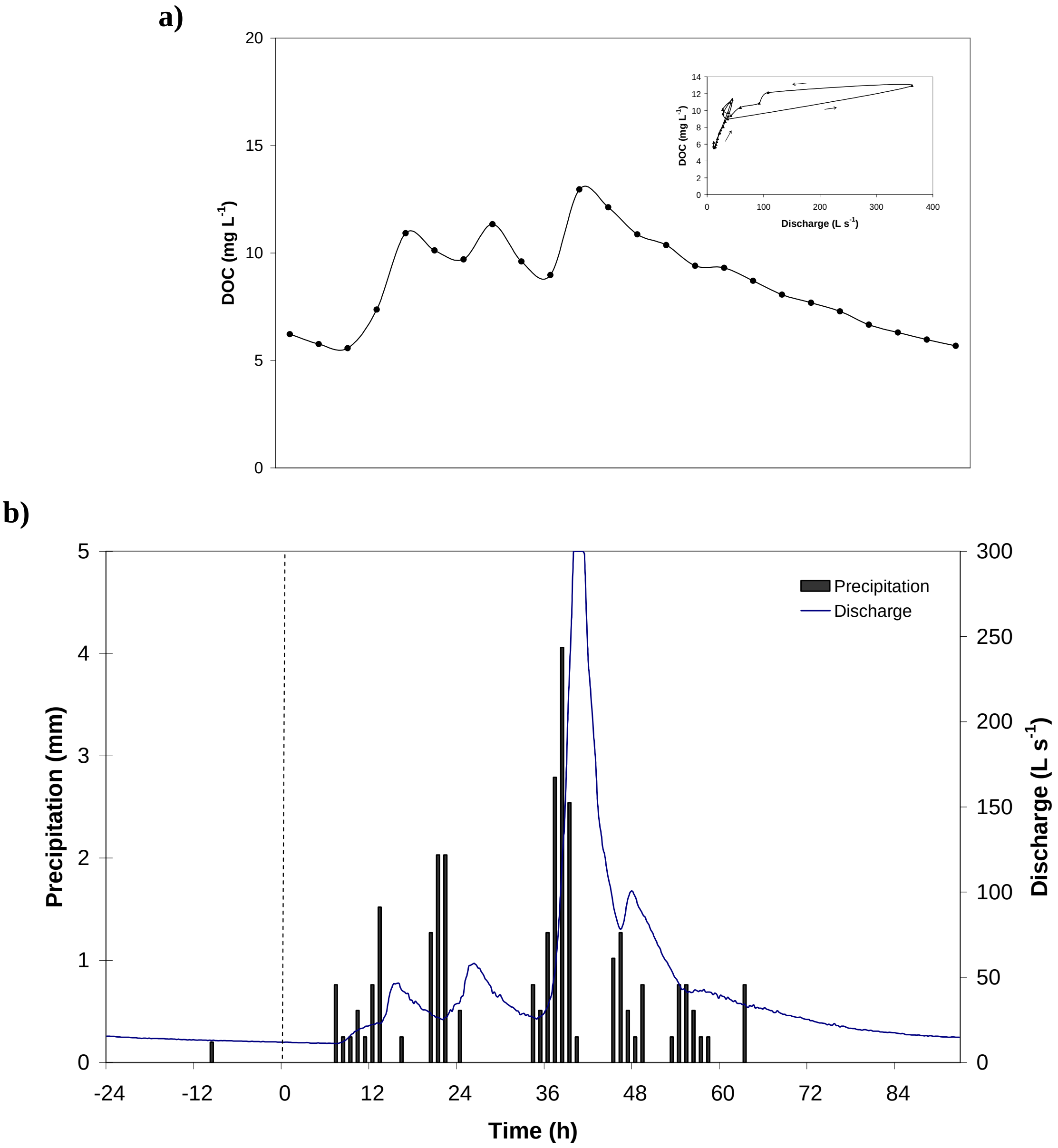


Figure 30: Variations at the Ochil Hills site of a) Dissolved Organic Carbon (DOC) concentrations (mg L^{-1}) taken at 4 hour intervals between 15.22pm on the 9th November and 11.22am on the 13th November 2005, inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}), and b) Discharge (L s^{-1}) and precipitation (mm) taken at 15 minute and 1 hour intervals respectively, between 15.22pm on the 8th November and 11.22am on the 13th November 2005.The dashed line illustrates when DOC sampling began.

A similar trend was observed during February 2005 (Figure 31). The antecedent conditions in the catchment were again wet, as twelve hours prior to the start of sampling; a storm hydrograph, with a discharge peak of 250 L s^{-1} was measured. The initial samples were taken on the falling limb of this storm hydrograph and exhibited a decreasing trend until the discharge increased rapidly producing a storm hydrograph with a discharge peak exceeding 300 L s^{-1}.

During this hydrograph, the DOC displayed anti-clockwise hysteresis, and DOC concentrations on the falling limb again remained high. However, the DOC concentrations did show signs of becoming exhausted as prior to the discharge peak, on the falling limb of the previous storm hydrograph at a discharge of 29.07 L s^{-1}; DOC concentrations measured 5.97 mg L^{-1}. However, at a similar discharge (29.32 L s^{-1}) after the discharge peak measured in this event, the DOC concentration was only 4.87 mg L^{-1}.

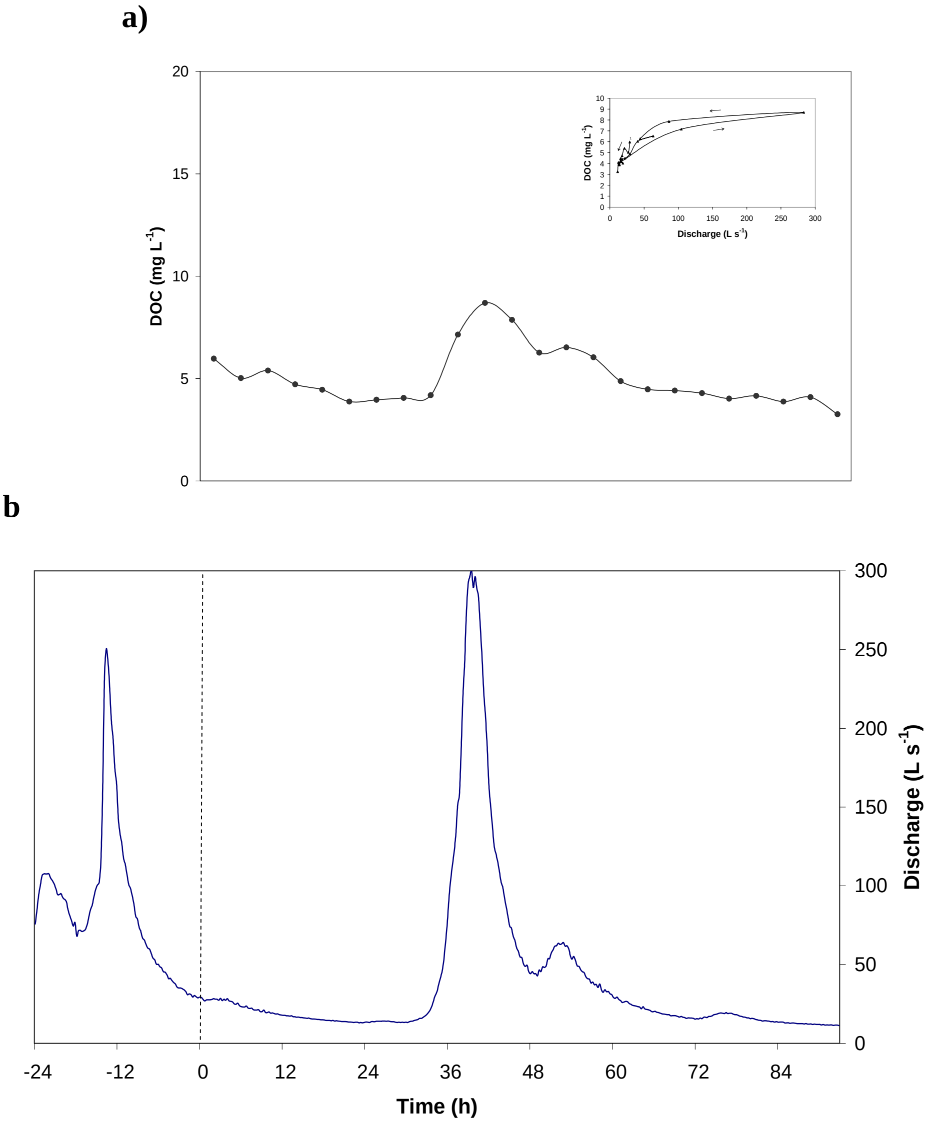


Figure 31: Variations at the Ochil Hills site of a) Dissolved Organic Carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals between 12.40pm on the 10th February and 08.40am on the 14th February 2005, inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}) and b) Discharge (L s^{-1}), taken at 15 minute intervals between 12.40pm on the 09th February and 08.40am on the 14th February 2005. The dashed line illustrates when DOC sampling began.

It has been previously identified that during storm events, the initial DOC concentrations measured within the stream are from water within the deep soils, which is displaced by the incoming precipitation, resulting in low initial DOC concentrations. Concentrations were observed to increase on the falling limb of the hydrograph as the groundwater level increases and the water being moved from the soil is now also moving from the more organic horizons where DOC concentrations are higher (Evans *et al.,* 1999). This was observed to be occurring specifically in secondary storms following a period of dry antecedent conditions, where concentrations measured during the second storm hydrograph are greater then the first. However, during a large storm event, when the soil is already wet as shown by the November and February 2005 examples, the water will more rapidly increase in depth and accessing the sub-surface soil horizons where DOC concentrations are greater. Therefore greater concentrations of DOC measured within the stream. If the storm event continues it is potentially possible that if the soil becomes saturated then the runoff generation progresses to saturation excess, where overland flow occurs and the DOC concentrations will decrease as the storm event continues (Worrall *et al*., 2002). However, in sites where overland flow is limited such as the Ochil Hills site, then it is possible that exhaustion of DOC occurs (Worrall *et al* 2002), as was observed during the February 2005 event where the concentration of DOC measured prior to the discharge peak was higher (5.97 mg l^{-1}) than that measured after the discharge peak (4.87 mg l^{-1}), even though both samples were taken at similar discharges (34.67 L s^{-1} and 34.94 L s^{-1}). The exhaustion of DOC may however be also related to season, which will be discussed further in the next section.

4.5 Seasonality of the dissolved organic carbon/discharge relationship

In addition to the hysteresis effects, seasonal differences in DOC production may account for the scatter around the regression line of the DOC/log Q relationship, shown in Figure 20, as temperature has been identified as a control of DOC production (Andersson *et al.*, 2000;Andersson and Nilsson, 2001; Neff and Hooper, 2002). To examine the seasonal variation in the data collected, all dissolved organic carbon (DOC) concentrations, corresponding discharges, air temperatures and continuous discharge data were divided into seasons (Wilby, 2001; Tank *et al.*, 2005; Pauling and Paeth, 2007), data were thus divided into spring (March-May), summer (June-August), autumn (September-November) and winter (December-February), a summary of these data is shown in Table 8, which shows that a wide range of DOC concentrations (1.68-21.1 mg L^{-1}) were measured within the Ochil Hills stream. The mean, median and range of DOC concentrations measured were also found to vary with season. The highest mean and median were measured during the autumn and the largest range of DOC concentrations were measured during the autumn and summer. However, the summer mean and median concentration were low, and similar to the spring. The winter's mean and median were greater than the spring and summer, but a reduced range of concentrations were measured during the winter. Air temperatures measured concurrently with DOC samples, were found to vary with season. The highest temperatures were measured during the summer, then the autumn, and lower temperatures were measured during the spring and winter. The discharges that were sampled during this study (instantaneous discharge) are representative of all discharges that were measured within the Ochil Hills catchment as similar overall mean, median and range of discharges were measured as shown in Table 8. Although a lower range of discharges were measured during the spring and autumn.

Table 8: The mean, median and ranges of dissolved organic carbon (DOC), discharge and temperature measured at the Ochil Hills site during spring, summer, autumn and winter and the overall mean, median and range.

Season	Descriptive Statistics	DOC (mg L^{-1})	Air Temperature (°C)	Instantaneous Discharge ($L\ s^{-1}$)	All Discharges ($L\ s^{-1}$)
Spring	Mean	3.32	4.35	17.23	19.81
	Median	2.43	4.75	5.87	9.291
	Range	1.71 – 8.81	-1.75 – 12.65	4.54 – 164.93	1.07 – 300
		(n=47)	(n=47)	(n=47)	(n=4616)
Summer	Mean	3.99	11.93	7.96	6.7
	Median	2.36	11.65	3.63	3.08
	Range	1.68 – 18.31	6.50 – 21.30	2.47 – 124.73	1.76 – 137.65
		(n=72)	(n=72)	(n=72)	(n =3486)
Autumn	Mean	6.60	9.03	18.06	23.74
	Median	5.42	9.125	9.67	9.93
	Range	2.66 – 21.1	-0.15 – 16.3	2.77 – 221.25	1.90-300
		(n=168)	(n=82)	(n=168)	(n=15593)
Winter	Mean	5.13	3.822	24.68	22.77
	Median	4.31	4.28	14	9.29
	Range	2.22 – 11.43	-4.15 – 8.6	5.14 – 283.33	4.88 – 300
		(n=183)	(n=120)	(n=183)	(n=14502)
Total	Mean	5.32	7.07	19.01	21.34
	Median	4.44	7.05	8.98	8.92
	Range	1.68 - 21.1	-4.15 – 21.3	2.47 – 283.33	1.07-300
		(n=470)	(n=321)	(n=470)	(n=38197)

To examine the seasonal patterns in the relationship between DOC concentrations and the log of discharge (log Q), the Pearson's product moment correlation coefficient was calculated for each season. The strongest correlation was identified during the summer (r =0.975, df =70, P<0.01) and autumn (r =0.864, df =166, P<0.01), but strong correlations were also found within the spring (r =0.818, df =45, P<0.01) and winter (r =0.812, df =181, P<0.01). The strength of the relationships can be observed in the scatterplots shown in Figure 32 and in the regression equations in Table 9. Similar slopes of the regression line are seen in the winter and spring, and the summer and autumn, however much steeper slopes are seen in the summer and autumn. When the scatterplots are examined more closely, considerable scatter is observed around the autumn regression line, which suggests a second DOC/discharge relationship. It is therefore suggested, that the seasonal differences in the DOC/discharge relationship are weakening the overall relationship (R^2=0.59), and may provide an additional explanation for the scatter around the regression line in Figure 20.

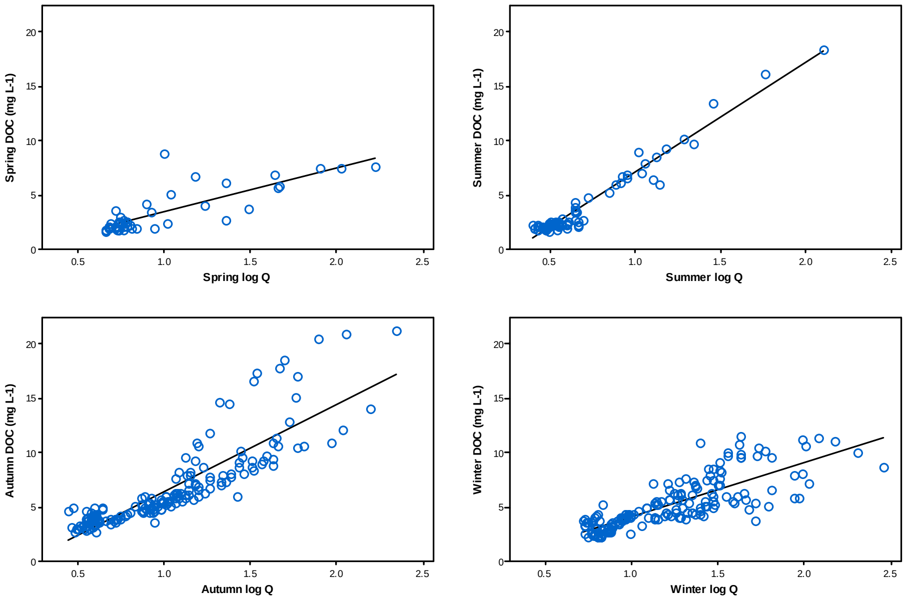


Figure 32: Scatterplot of dissolved organic carbon (DOC) plotted against the log of discharge, separated by season (autumn, spring, summer and winter).

Table 9: Summary table of seasonal and overall regressions of DOC (mg L^{-1}) on discharge (Q), produced from data collected from the Ochil Hills site between 2004 and 2006.

Season	**Seasonal regression equations** **(coefficients ± standard error)**	**R^2**
Spring	DOC = - 0.550 + 4.00 log Q ±0.44 ±0.42	0.67
Summer	DOC = - 2.96 + 10.1 log Q ±0.21 ±0.28	0.95
Autumn	DOC = - 1.57 + 7.99 log Q ±0.40 ±0.36	0.75
Winter	DOC = - 0.870 + 4.99 log Q ±0.34 ±0.27	0.66
Overall	DOC = -0.851 + 5.94 log Q ±0.26 ±0.23	0.59

4.5.1 Summer (June – August)

A strong relationship was identified between DOC and the log of discharge during the summer (R^2= 0.95). It can however be identified that during the summer there are two distinct patterns of DOC release which is dependent on flow. The low mean and median DOC concentrations measured during the summer show that the majority of the samples were of low concentration and as was discussed previously, the low concentrations were measured during baseflow conditions (the main flow condition during the summer) when the principal source of DOC, was the groundwater which contains low DOC concentrations. This trend observed during the summer has been observed within other catchments; Mulholland and Hill (1997) identified that >65% of the stream discharge during the summer came from the bedrock zone. Concentrations of DOC greatly increased during storm events when the principal source of DOC was not the groundwater, as was observed during the August 2005 storm event (Figure 25), where a peak

DOC concentration of 18.3 mg L^{-1} was measured. High concentrations of DOC have been identified in other studies occurring during storm events in the summer (Grieve, 1994). The high concentrations occur because DOC production within the summer months is high, due to increases in temperatures which promotes increased DOC production by the soil biota (Cole *et al.*, 2002). This accumulates in the soil until a precipitation falls on the site to move it to the stream. This is supported by the DOC/discharge regression equation, as the summers slope value is the largest of all the seasons, therefore more DOC is available at the same unit discharge during the summer than the other seasons.

4.5.2 Autumn (September – November)

A strong relationship was identified between DOC and the log of discharge during the autumn ($R^2 = 0.75$). The autumn period also had the highest mean, median and range of DOC concentrations. The high concentrations of DOC measured during the autumn, have been observed in this (Grieve, 1984a) and other catchments (Worrall *et al.*, 2002), and were due to an accumulation of DOC during the summer months, which were then flushed from the soil during the autumn, and indeed the mean and median autumn discharges in the Ochil Hills catchment were higher than those measured than during the summer. When the regression equation is analysed for the autumn, it can be observed that the slope of the regression is not as steep as during the summer, although higher concentrations were measured during the autumn, however it is suggested that the reduced slope of the regression is influenced by the two relationships that were observed in the scatterplot (Figure 32), which may represent a depletion of DOC as the autumn progresses.

4.5.3 Winter (December – February)

A strong relationship was identified between DOC and the log of discharge during the winter (R^2= 0.66). The highest mean and median discharges were measured during the winter period. However, the range of DOC concentrations was lower than both the autumn and summer, although the median DOC winter concentration was higher than the summer median (due to the high number of base flows measured during the summer). This would suggest that the high concentrations of DOC, measured particularly during the previous autumn period, resulted in an exhaustion of DOC as the discharge was high throughout the winter period. This exhaustion effect was observed specifically within the sampling set from February 2005 (Figure 31). Where prior to the discharge peak, at a discharge of 34.67 L s^{-1}, DOC concentrations measured 5.97 mg L^{-1}, however, at a similar discharge (34.94 L s^{-1}) after the discharge peak, the DOC concentration was only 4.87 mg L^{-1}. DOC exhaustion may occur throughout the year, however, during the previous study within the Ochil Hills catchment, a similar reduction in DOC concentrations during the winter corresponding to high discharges was observed, perhaps due to an exhaustion of the DOC or reduced organic activity during the winter (Grieve, 1984b). This is also supported by the reduced steepness of the slope value within the winter regression equation, when compared to the summer and autumn.

4.5.4 Spring (March – May)

A strong relationship was identified between DOC and the log of discharge during the spring (R^2= 0.67). The lowest mean DOC concentration and the smallest range of DOC concentrations were measured during the spring. The low concentrations measured is because the soil DOC store was already depleted during the winter, and because of the limited microbial activity during the cold winter and early spring months, when there is less DOC available. This is confirmed by the fact that the mean and median discharges measured during the spring were similar to the winter and autumn. The slope value of the spring DOC/discharge regression relationship was also the lowest of all the regression relationships, suggesting that the spring is when the DOC stores are most depleted. The focus of many studies examining the seasonality of DOC concentrations within water bodies during the spring months is to investigate the influence of the spring snowmelt on the concentration of DOC. Typically in high elevation catchments, where the ground is covered with snow during the winter months, spring maxima DOC are observed (McKnight and Bencala, 1990; Boyer *et al*., 1997; Brooks *et al*., 1999). DOC accumulates during the winter, subsequently when the snow melts during the spring the water table rises and flow increases through the upper soil horizons (Boyer *et al*., 1997). High concentrations of DOC are then flushed from the soil, and Brooks *et al.* (1999) observed that 70-80% of the annual export of DOC occurred in the three months after the spring melt with the highest DOC concentrations occurring within the first snowmelt. In individual locations it has been observed that accumulated DOC can be flushed from the soil within 10-30 days (Boyer *et al*., 1997). However, as there was limited snowfall at the Ochil Hills site, this model of changing DOC concentrations during the spring is not applicable to this catchment, which would explain why no such dramatic increase in DOC concentration was measured.

4.6 Summary

A strong relationship was identified between dissolved organic carbon (DOC) and the log of discharge (log Q) within the Ochil Hills catchment (R^2 =0.59). This indicates the importance of the relationship between the hydrology of the catchment and the concentration of DOC that was measured within the stream. Low DOC concentrations were measured when there was no or limited precipitation inputs in the catchment, as the source of DOC was the groundwater where DOC concentrations are low. DOC concentration increased during storm events following both dry and wet antecedent conditions within the catchment and anti-clockwise hysteresis was observed during the majority of storm events, suggesting that the sources of DOC were both from the immediate area and further within the catchment and limited exhaustion of DOC was identified. When individual sampling events were examined, it was identified that the antecedent conditions in the catchment controlled the hydrological flow paths that were followed to the stream thus altering the concentration of DOC measured. Specifically how long the storm event lasted, the scale of the storm event and what the antecedent conditions were in the catchment. The importance of season in the relationship between the DOC concentration and the catchments hydrology was identified when the DOC/discharge data was sub-divided into season, which produced in increase in the strength of relationship during the summer (R^2=0.95), autumn (R^2=0.75), spring (R^2=0.67), winter (R^2=0.66). The greatest DOC concentration was measured during the summer after a period of limited rainfall. The mean DOC concentration was greatest during the autumn, corresponding to the increase in discharge within the catchment when compared to the summer. Concentrations were lower in the spring and winter, due to decreased production of DOC, although the median DOC concentration in the winter was higher than in the summer, which is perhaps because of the greater number samples taken during low flows in the summer.

Chapter 5 - Duchray Catchment

5.1 Introduction

The aim of chapter 5 is to describe and discuss the results from the Duchray catchment within the Loch Ard site, focussing on the relationship between dissolved organic carbon (DOC) concentrations and discharge. The specific aim is to establish potential controls of DOC concentrations within the Duchray catchments, objective 1 of this research, and to test the hypothesis that temperature and the hydrology of the catchment are the main drivers of short term changes in DOC concentrations in the Duchray catchment. The DOC results discussed in this chapter are from samples taken from the Duchray catchment between 30th June 2004 and 27th January 2006; a total of eighteen sample sets were taken at four hour intervals. The total number of samples used within the analysis of the results was 355.

5.2 Overview of results from the Duchray catchment

Figure 33 gives an overview of the results collected from the Duchray catchment. This shows all precipitation, discharge and dissolved organic carbon (DOC) results collected. It can be seen in Figure 33, that a good relationship exists between precipitation and discharge. This would be expected, but there is potential for inconsistencies between the two data sets, as the precipitation record was from a raingauge approximately 9 km South-East of the catchment, which captures the majority (90-95%), but not all the precipitation falling on the Duchray catchment (SEPA, personal communication). DOC concentrations show pronounced seasonal variations, with the highest concentrations measured in June, August and September 2004. During 2005, DOC concentrations were lower, the highest concentrations were again measured during the summer (July and August) and autumn (September and October) and the lowest DOC concentrations were measured during the winter (January and February) and early spring (March and April).

Figure 33 clearly identifies the potential importance of season in altering the concentration of DOC measured within the catchment. However, what is less clear is the relationship between DOC concentration and discharge. Although seasonal patterns exist, concentrations of DOC measured during July of both years were lower than other events sampled during the summer period, suggesting that the season is not the only factor effecting change in DOC concentration. To examine the relationship more closely, the overall DOC/discharge relationship was analysed, then the individual seasonal DOC/discharge relationships were investigated.

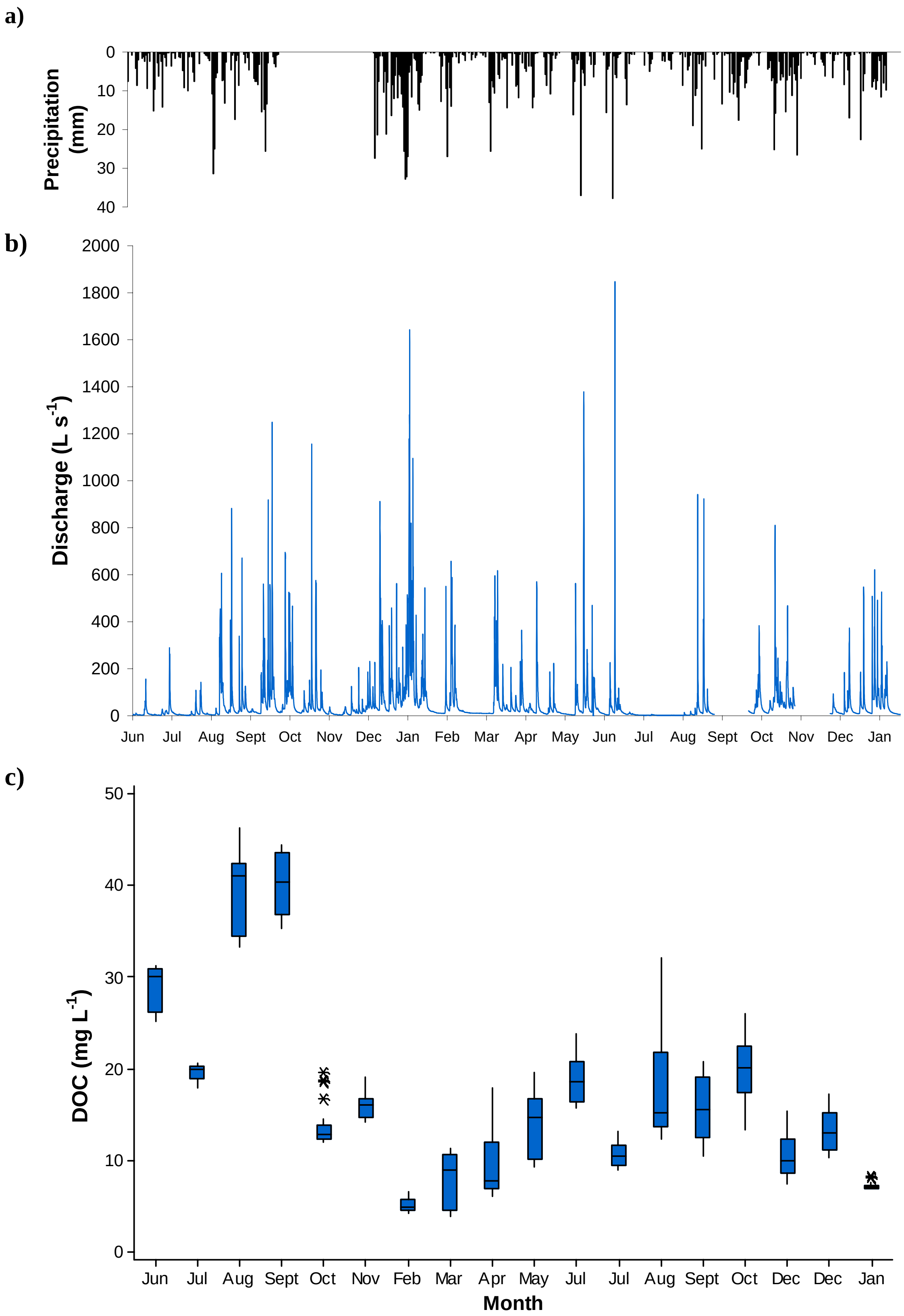


Figure 33: All measurements taken at the Duchray catchment of a) Daily precipitation (mm) (data missing between 29th September and 12th December 2004), b) Average hourly discharge (L s^{-1}) (data missing between the 6th September and 3rd October 2005 and the 9th November and 7th December 2005) and c) Boxplots showing 18 sample sets of dissolved organic carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals, between June 2004 and January 2006.

5.3 DOC/discharge relationship in the Duchray catchment

To examine the relationship between DOC concentration and the corresponding instantaneous discharge in the Duchray catchment, the Pearson's product moment correlation coefficient was calculated (all discharges were logged prior to the calculation). A weak positive correlation was identified between DOC and the log of discharge ($r = 0.218$, $df = 353$, $P<0.01$), as the two variables had only 4.5% of their variation in common. The relationship between DOC and the log of discharge is shown in Figure 34.

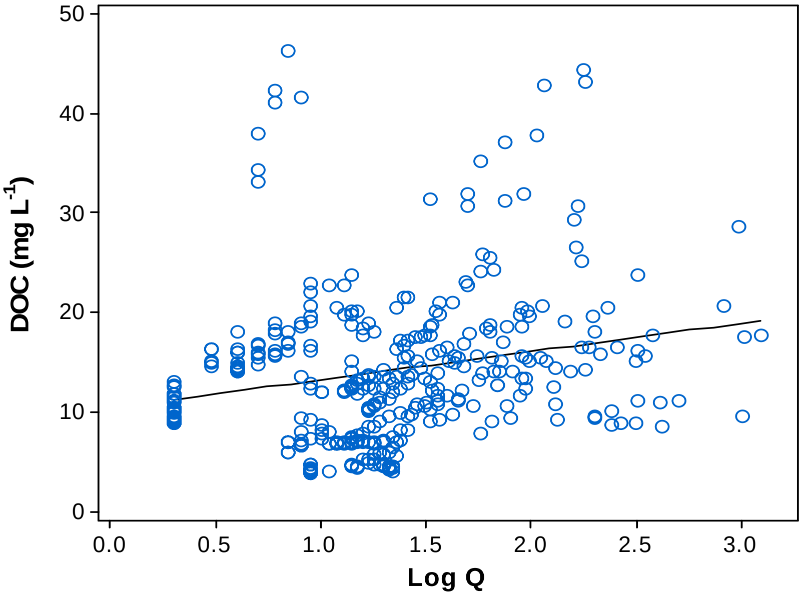


Figure 34: Scatterplot showing the relationship between dissolved organic carbon (DOC) and the log of discharge (log Q) ($R^2 = 0.048$), in the Duchray catchment between the 30th June 2004 and the 27th January 2006.

This weak relationship, contrasts with the strong positive relationship, identified between DOC and the log of discharge within the Ochil Hills catchment, identified in this study, and also in other upland catchments (Worrall *et al.*, 2002). However, a weak relationship ($R^2 = 0.095$) was identified in the previous study in the Duchray catchment (Grieve 1994) and other research in forested catchments have found both weak ($R^2 = 0.09$) (Bernal *et al.*, 2002) and strong relationships ($R^2 > 0.7$) (Hinton *et al.*, 1997) between DOC and the discharge during storm events. The relationship between DOC and discharge was improved in Bernal *et al.'s* (2002) study ($R^2 = 0.65$) when only high flows were used. This suggests that when samples are taken throughout the seasons at a range of discharges the relationship between DOC and discharge can be poor, which may account for the poor relationship between DOC and the log of discharge within the Duchray catchment. Therefore the relationship between DOC and discharge will be examined under different flow conditions.

5.3.1 DOC relationship with low discharge

It can be observed in Figure 34 that there is a weak relationship between dissolved organic carbon (DOC) and discharge in the Duchray catchment. During periods of low discharge, large variations in DOC concentrations were found, and some high DOC concentrations were measured, for example in August 2004, DOC concentration of between 33.26 and 46.35 mg L^{-1} were measured during low discharges ranging from 5 to 8 L s^{-1}. The high DOC concentrations measured within the Duchray catchment, contrasts with the generally low concentrations measured within the Ochil Hills catchment, when low discharges dominated.

To examine the relationship between DOC and discharge when low discharges dominate, two sampling events from July 2005 (Figure 35) and November 2004 (Figure 36) were examined, prior to both the sampling events dry antecedent conditions existed within the catchment. Discharges within the Duchray stream were low in both the July 2005 (2 L s^{-1}) and November 2004 (3-7 L s^{-1}) sampling events, yet DOC concentrations varied in July 2005 (8.97-13.23 mg L^{-1}) and November 2004 (14.18 and 19.03 mg L^{-1}). When the events are examined more closely, the factors controlling the differences in DOC concentrations can be identified. During July 2005 when discharges remained at 2 L s^{-1}, DOC concentrations were shown to decrease from the first (13.23 mg L^{-1}) to the last sample (10.01 mg L^{-1}). It is therefore suggested, that prior to this event was sampled, DOC concentrations within the baseflow were high. High DOC concentrations within the baseflow would be expected, if precipitation had fallen on the catchment and moved high DOC concentrations from the upper soil horizons to the lower soil horizons. In the 5 days prior to this event was sampled, only 4.8mm of precipitation fell on the catchment, therefore high concentrations of DOC must have been available for movement from the upper soil horizons, as the concentration of DOC moved to the lower horizons would decrease due to DOC adsorption in the mineral soil of the Duchray catchment (McDowell and Wood, 1984; Jardine *et al*., 1989; Moore *et al*., 1992).

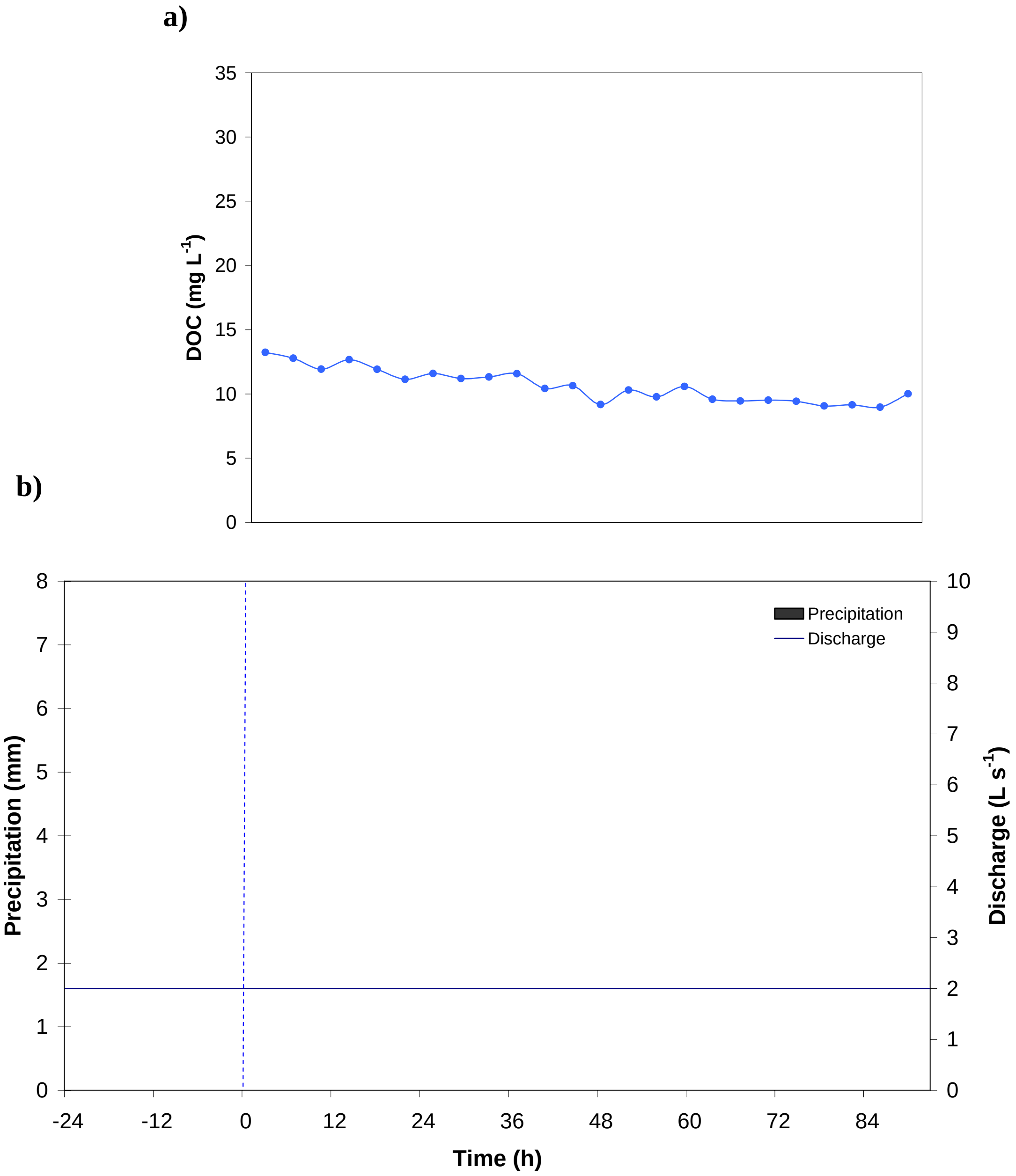


Figure 35: Measurements at the Duchray catchment of a) Dissolved organic carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals between 11.00 am on the 24th July and 7.00 am on the 28th July 2005 and b) Discharge (L s^{-1}) measurements taken at 15 minute between 11.00 am on the 23rd July and 7.00 am on the 28th July 2005. The dashed line illustrates when DOC sampling began.

During the July 2005 event, a general decrease in DOC concentration was observed. However, small fluctuations in DOC concentrations were also seen, which could be due to in-stream processing and diel changes in DOC concentrations, as were discussed in section 4.4.1.1. However as was observed in the Ochil Hills stream, there is little evidence to support major diel fluctuations and there is a limited control of in-stream processing as peak DOC concentrations were observed during the night, when previous research has found peak DOC concentrations during the late afternoon (Kaplan and Bott, 1982).

During the November 2004 sample set, a different pattern emerged, as fluctuations in DOC concentrations were observed to correspond to small changes in discharge. This can specifically be observed at the end of the sampling set, where DOC concentrations increase from 16.89 to 19.03 mg L^{-1}, as discharge increase from 5 to 6 L s^{-1} and the DOC concentration remained high in the last two samples, as the discharge increased to 7 L s^{-1}.

When two events are compared it can also be observed that the baseflow and DOC concentrations were higher in the Duchray catchment during the November 2004 event than the July 2005 event. This corroborates previous research that has identified that during the summer months the stream discharge is generated from the bedrock, however during the cooler months when there is more precipitation, the water supplying the stream is generated from the saturated groundwater above the bedrock where DOC concentrations are higher (Mulholland and Hill, 1997).

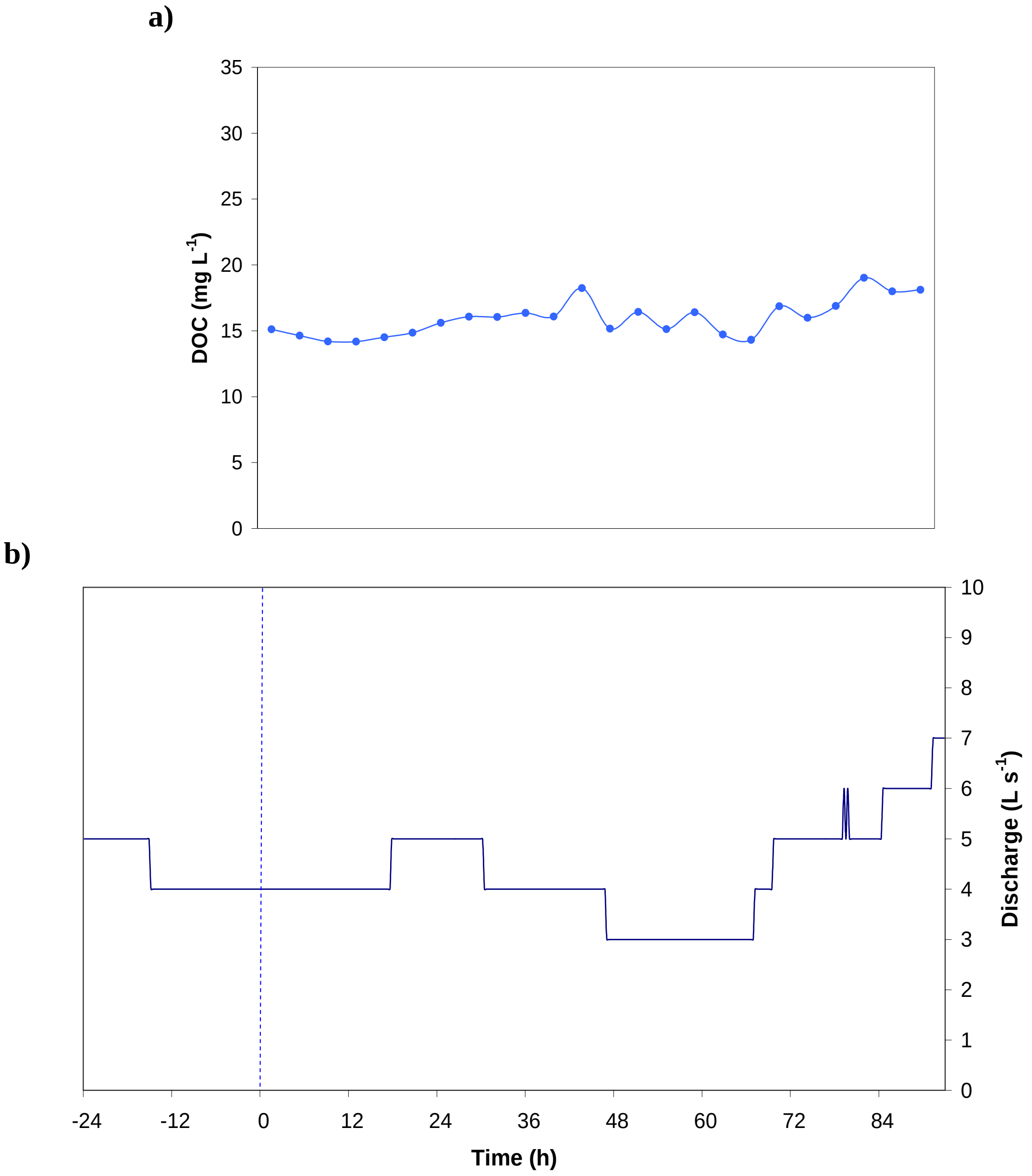


Figure 36: Measurements at the Duchray catchment of a) Dissolved organic carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals between 13.00 pm on the 11th November and 9.00 am on the 15th November 2004 and b) Discharge (L s^{-1}) measurements taken at 15 minute between 13.00 pm on the 10th November and 9.00 am on the 15th November 2004. The dashed line illustrates when DOC sampling began.

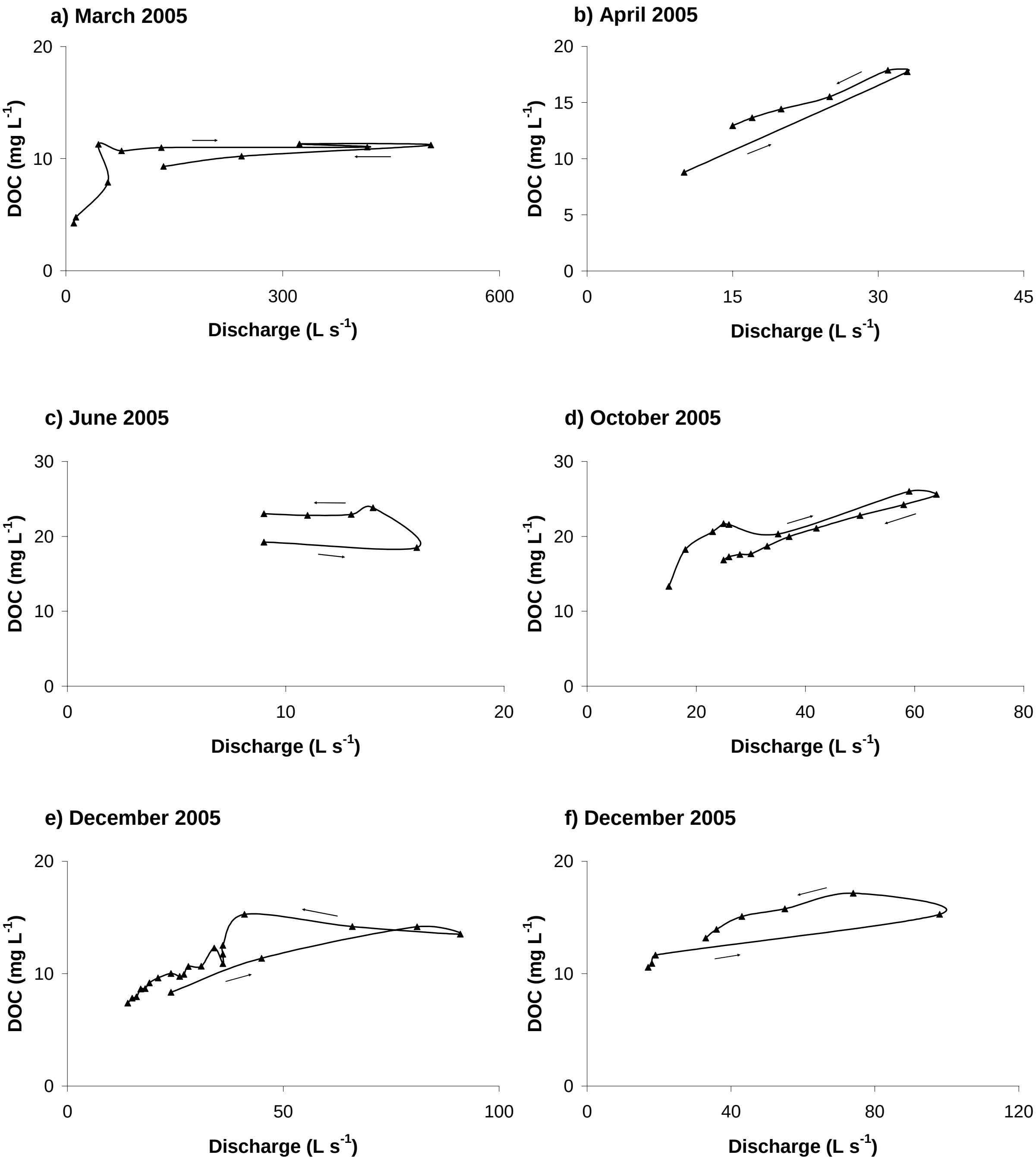
Analysis of the baseflow sample sets identified that the hydrology of the catchment is an important control of DOC concentrations even when discharges are low. This was specifically observed during the November 2004 event where small changes in discharge produced more substantial changes in DOC concentration.

5.3.2 DOC and storm events

It has been identified that when no precipitation is falling on the Duchray catchment, the concentrations of dissolved organic carbon (DOC) measured within the stream varies because of changing DOC concentrations within the groundwater, which is the principal source of water to the stream under baseflow conditions. However, this variation in DOC concentrations can also be observed during higher discharges as shown in Figure 34. To identify the reasons behind these variations in DOC concentrations, then this section aims to identify how hydrological processes within the catchment are controlling the DOC concentrations measured within the stream during storm events. This will be achieved as discussed in section 4.4.2 by identifying the antecedent conditions in the catchment prior to the storm event, considering the length and intensity of the precipitation and examining how DOC concentrations change during storm events, to potentially identify the flow sources of the DOC. Initially DOC concentrations will be plotted against discharge to identify if DOC hysteresis is occurring and the direction of the hysteresis. In addition a selection of storm events will be analysed to identify how the final DOC concentration is controlled by the catchments hydrology.

5.3.2.1 Dry antecedent conditions

When dissolved organic carbon (DOC) was plotted against discharge during storm events sampled following dry antecedent conditions (Figure 37), it can be observed that anti-clockwise hysteresis dominates. However, during March and October 2005 clockwise hysteresis was observed, but DOC concentrations were similar on the rising and falling limbs. It would be expected that if the soil was dry when precipitation fell on the catchment, then initial stream DOC concentrations would be high and clockwise hysteresis of DOC would take place, as flushing of soluble materials that had accumulated during the previous dry period would occur (Soulsby, 1995) and if the soil is very dry, infiltration excess overland flow will occur and high concentrations of DOC from vegetation throughfall will be moved directly overland to the stream (Soulsby, 1995). The dominance of the anti-clockwise hysteresis suggests that the initial low concentrations of DOC were due to the displacement of the groundwater by the incoming precipitation, as the storm progressed then higher DOC concentrations were measured on the falling limb, as precipitation that had moved through the upper soil horizons, was DOC enriched and therefore higher DOC concentrations were measured within the stream (Evans *et al.*, 1999), producing the anti-clockwise hysteresis observed. However, the hysteresis may also be dependent on the availability of the DOC within the catchment, for instance during the winter and spring months (April and December 2005), DOC production is limited, as are the accumulated stores of DOC available to be flushed from the soil. During October 2005, it is suggested that the soil store of DOC is greater, which would explain the limited clockwise hysteresis observed.


a) March 2005

b) April 2005

c) June 2005

d) October 2005

e) December 2005

f) December 2005

Figure 37: Hysteresis loops of dissolved organic carbon (DOC) plotted against discharge, during storm events following dry antecedent conditions in the Duchray catchment.

To further identify how specific hydrological processes control DOC concentrations, during storm events following dry antecedent conditions, a series of storm events were identified and evaluated. One hydrological factor that has been identified to control DOC concentration moved from the soil to the stream is the magnitude of the storm event. During March 2005 a large storm event with a peak discharge of 611 L s^{-1} was measured and is shown in Figure 38.

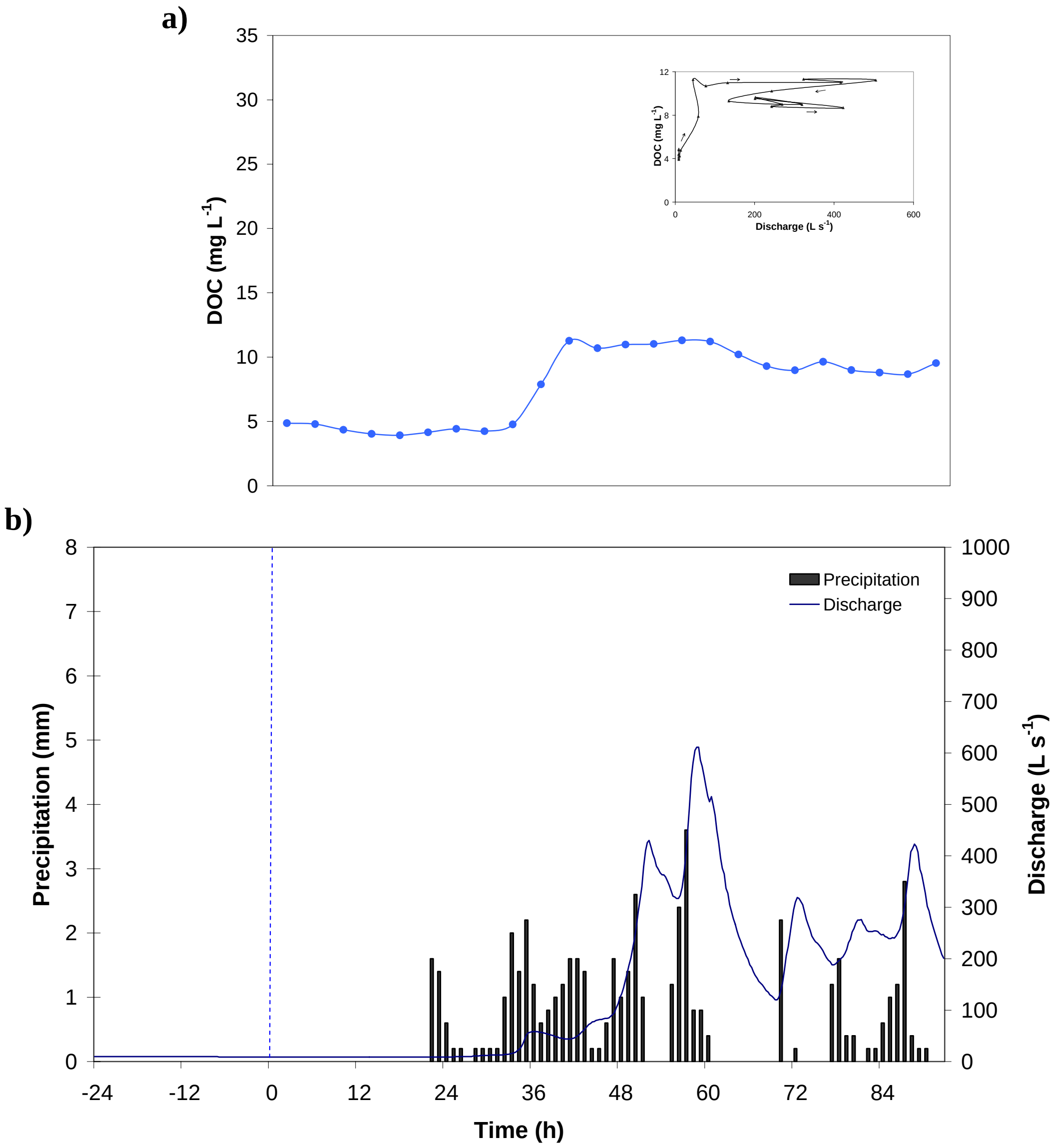


Figure 38: Measurements at the Duchray catchment of a) Dissolved organic carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals between 11.00 am on the 13th March and 07.00 am on the 17th March 2005, inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}), and b) Discharge (L s^{-1}) and precipitation (mm) taken at 15 minute and 1 hour intervals respectively, between 11.00 am on the 12th March and 07.00 am on the 17th March 2005. The dashed line illustrates when DOC sampling began.

The event extended over three days, 51.4mm of precipitation fell and discharge did not return to base flows. Prior to precipitation inputs, low DOC concentrations (3.94 - 4.87 mg L^{-1}) were measured. Concentrations increased as precipitation fell, and on the falling limb of the first small storm hydrograph, with a peak discharge of 58 L s^{-1}, the second highest DOC concentration (11.27 mg L^{-1}) was measured and anti-clockwise hysteresis was observed. Although precipitation continued to fall on the site and two large discharge peaks (430 L s^{-1} and 611 L s^{-1}) were measured, DOC concentrations exhibited only small variations with discharge and stayed fairly constant (10.69 - 11.31 mg L^{-1}). During a series of smaller storm hydrographs with peak discharges of 319 L s^{-1}, 276 L s^{-1} and 423 L s^{-1} DOC concentrations again showed some small variation with discharge but stayed fairly constant (8.68 - 9 mg L^{-1}). It is has been identified in the March 2005, that although this storm event was of high magnitude the concentration of DOC available for movement from the Duchray catchment is limited as the peak concentration was maintained during the storm event and eventually decreased as the storm event continued. However, the scale of the exhaustion of DOC was still limited, as higher DOC concentrations were measured at the end of the event, then during baseflows at the beginning of the event. It should also be noted that the range of concentration measured within this storm event was small, which is perhaps because of the reduced production of DOC during the winter months.

The event that was sampled during early December 2005 (Figure 39) shows that DOC concentrations in the Duchray catchment can rapidly increase during a storm event. This event was smaller in magnitude then the March 2005 event, as only one storm hydrograph with a peak discharge of 93 L s^{-1} was measured, but higher DOC concentrations were measured (7.38 to 15.29 mg L^{-1}). During the storm hydrograph the rapid increase in DOC concentration can be observed where the first sample taken on the rising limb at a discharge of 24 L s^{-1}, measured 8.34 mg L^{-1}, the concentration increased rapidly to 14.18 mg L^{-1}, two hours prior to the peak flow at a discharge of 91 L s^{-1}. The DOC did exhibit anti-clockwise hysteresis during this event, although two hours after the peak the concentration decreased to 13.51 mg L^{-1} at a discharge of 81 L s^{-1}, but the next sample taken increased to 14.2 mg L^{-1}, at a discharge of 66 L s^{-1}. It should be noted that the direction of the hysteresis was difficult to identify, as the next sample decreases to 8.13 mg L^{-1}, and is perhaps erroneous. Following the storm hydrograph, after discharge had returned to baseflows, the DOC concentration had decreased to 7.38 mg L^{-1}, which was lower then the initial concentration of 8.34 mg L^{-1}, although also at a lower discharge (14 L s $^{-1}$). This would suggest that some exhaustion of DOC is occurring within the catchment.

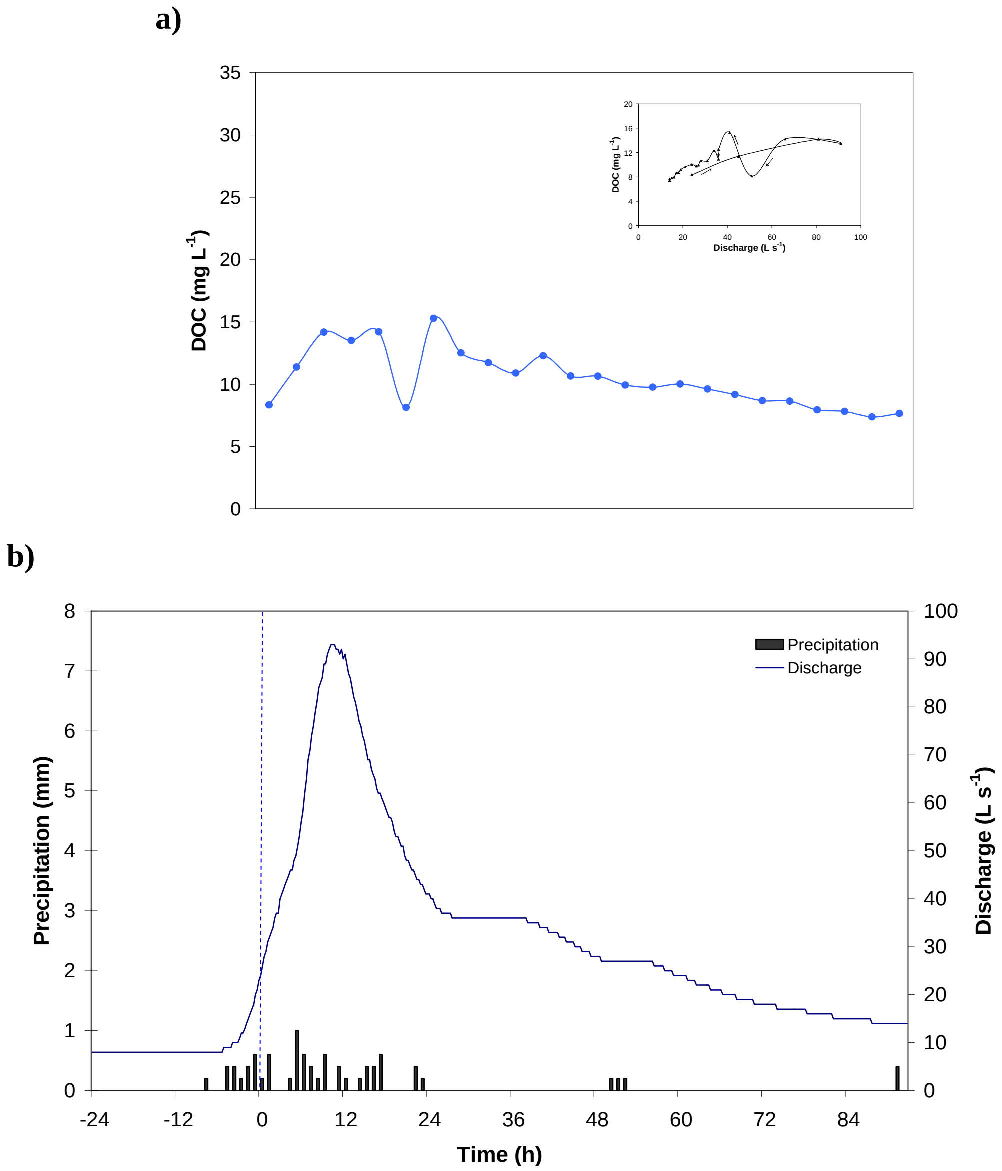


Figure 39: Measurements at the Duchray catchment of a) Dissolved organic carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals between 12.00 am on the 9th December and 9.30 am on the 13th December 2005, inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}), and b) Discharge (L s^{-1}) and precipitation (mm) measurements taken at 15 minute and 1 hour intervals respectively between 12.00 am on the 8th December and 9.30 am on the 13th December 2005. The dashed line illustrates when DOC sampling began.

To further examine if exhaustion of DOC is occurring within the Duchray catchment, then the sample set taken during October 2005 (Figure 40) was examined, where two storm hydrographs were sampled. During the nine hours prior to the start of the sampling period, 4 mm of precipitation fell on the catchment, which produced a slow increase in discharge from the baesflow of 11 L s^{-1} to 15 L s^{-1} when the first sample was taken, which had a DOC concentration of 13.31 mg L^{-1}. Subsequent concentrations increased rapidly, as the concentration of the next sample taken was 18.24 mg L^{-1} at a discharge of only 18 L s^{-1}. Further precipitation (2.2mm) produced a more rapid increase in discharge, producing a storm hydrograph with a peak discharge of 65 L s^{-1}, ~two hours prior to the peak at a discharge of 59 L s^{-1}, the peak concentration of DOC in this sample set was measured (26 mg L^{-1}), and slight clockwise hysteresis of the DOC was observed, although a similar concentration (25.61 mg L^{-1}) was measured during the peak of the storm hydrograph at 64 L s^{-1}. DOC concentrations and discharge subsequently decreased and it was not until further precipitation fell on the catchment that DOC and discharge again increased. The entire second storm hydrograph was not sampled, however at a discharge of 67 L s^{-1}, DOC concentrations again increased to 24.34 L s^{-1}, a similar concentration to the peak concentration measured during the previous storm hydrograph (26 mg L^{-1}). This suggests that there is a large store of DOC available within the Duchray catchment, as the DOC exhibited limited exhaustion during this event. This may be because the initial storm event occurred after dry antecedent conditions and it was not until the second storm event that the soil became wet and different source areas, perhaps the highly organic sub-surface soil were being accessed, and also accessed more rapidly.

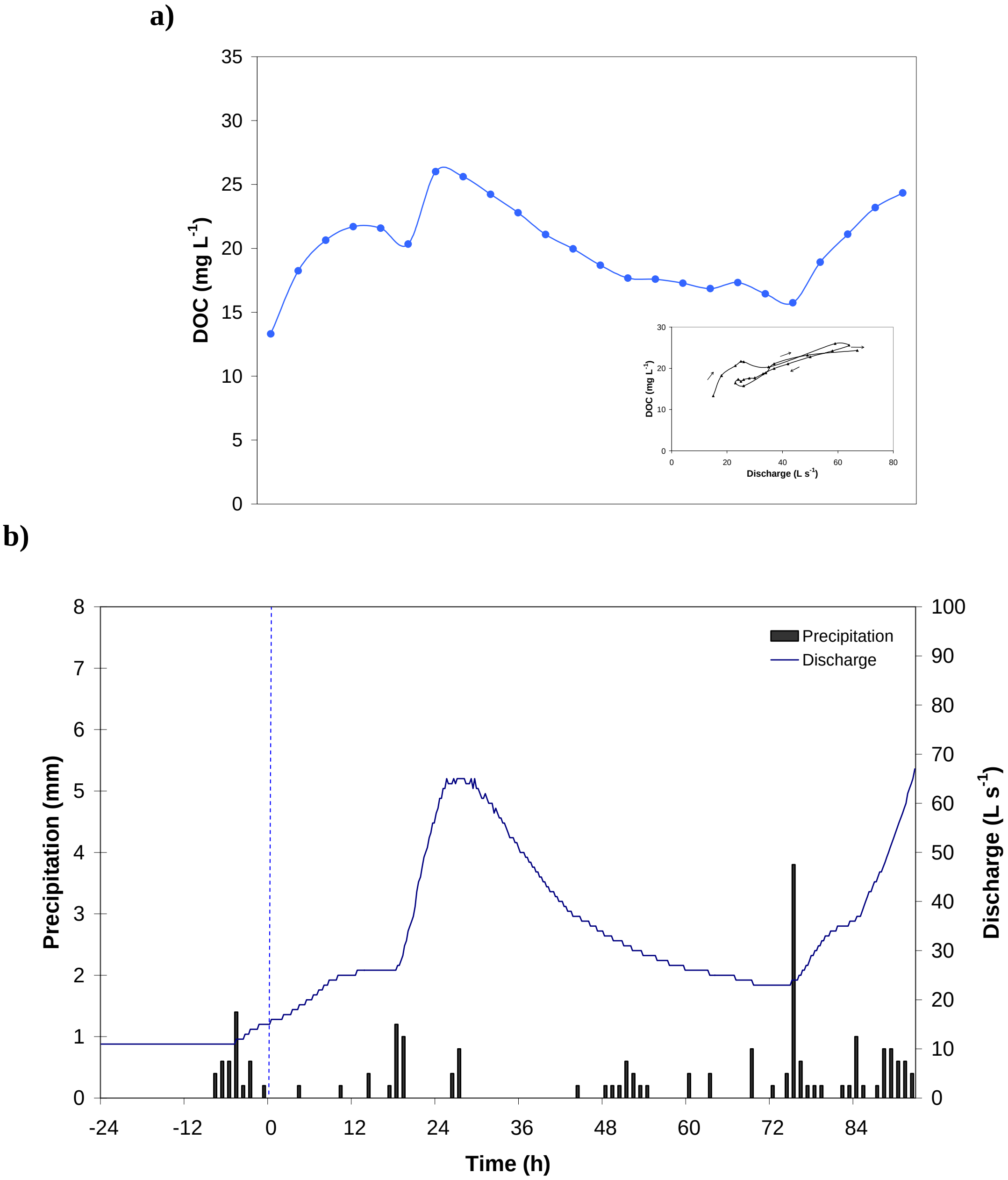
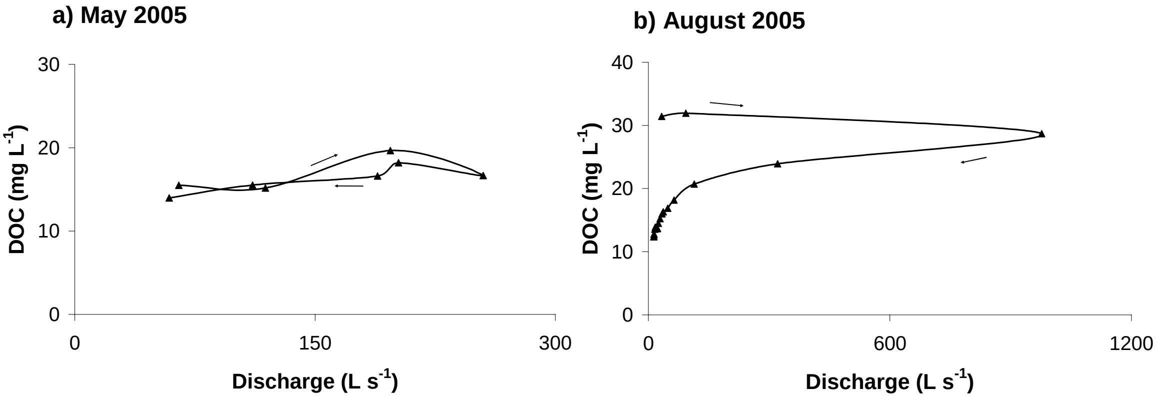


Figure 40: Measurements at the Duchray catchment of a) Dissolved organic carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals between 13.30 pm on the 19th October and 9.30 am on the 24th October 2005, inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}), and b) Discharge (L s^{-1}) and precipitation (mm) measurements taken at 15 minute and 1 hour intervals respectively between 13.30 pm on the 18th October and 9.30 am on the 24th October 2005. The dashed line illustrates when DOC sampling began.

5.3.2.2 Wet antecedent conditions

To identify how dissolved organic carbon (DOC) concentrations change during a storm event, following wet antecedent conditions within the catchment, a series of plots of DOC plotted against discharge were produced and are shown in Figure 41. The plots all show clockwise hysteresis of DOC concentration. However, in May 2005 the clockwise hysteresis observed was limited, as similar DOC concentrations were measured on the rising and falling limb of the storm hydrograph. It is suggested that clockwise hysteresis dominates because in many of the events the soil was previously wet, and a previous storm event had occurred, potentially depleting available DOC stores, thus higher concentrations are measured on the rising limb of the storm hydrograph, resulting in clockwise hysteresis. Alternatively, the concentration may be initially high because the flow path the water is following changes from sub-surface throughflow to overland flow, resulting in lower concentrations on the falling limb.



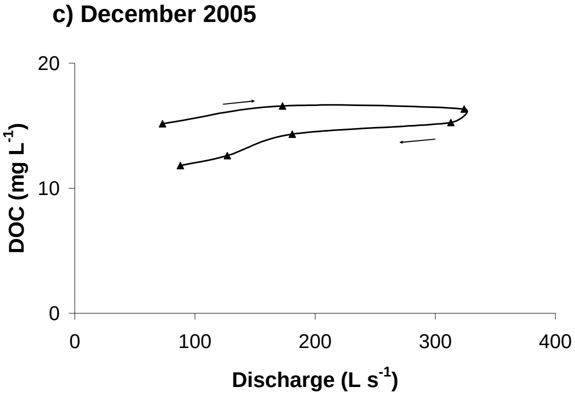


Figure 41: Hysteresis loops of dissolved organic carbon (DOC) plotted against discharge, during storm events following wet antecedent conditions in the Duchray catchment.

To further understand the hydrological processes that are controlling DOC concentrations during storm events following wet antecedent conditions, then three sampling sets taken during May, August and December 2005 will be discussed. During all the events, two storm hydrographs were monitored. Analysis of the events will be useful in identifying how the antecedent conditions within the catchment and the length of time between storm events influences the DOC concentration measured.

The initial storm hydrograph that was measured during the May (Figure 42) and December 2005 (Figure 43) followed limited precipitation during May (12.4 mm) and December (9mm). The storms were of different magnitude, as a larger discharge peak was measured in May (1484 L s^{-1}) than in December (107 L s^{-1}), yet the DOC exhibited anti-clockwise hysteresis. The largest increase in DOC concentration was measured during May 2005, increasing from 9.62 to 17.88 mg L^{-1} at similar discharges (1016 and 1253 L s^{-1}) on the rising and falling limbs of the storm hydrograph. In comparison a smaller increase in DOC concentration was measured during the December event, increasing from 15.29 to 17.16 mg L^{-1}, at similar discharges (98 and 74 L s^{-1}) on the rising and falling limbs of the storm hydrograph. During this initial storm event it is suggested that the different magnitude of the May and December 2005 events, could explain the disparity between DOC concentrations measured on the rising and falling limb of the storm hydrograph in the two events. Where potentially a greater volume of water was moving through the highly organic shallow sub-surface soil during the May 2005 event, than in December 2005 event due to the reduced precipitation, therefore DOC concentration were lower during December 2005 because the water level did not move up to the shallow-subsurface. The rapid decrease in DOC concentrations following the greater magnitude May 2005 event, may be due to a saturation of the soil where overland flow is contributing the majority of the water to the stream, resulting in lower DOC concentrations (Soulsby, 1995). However, if the soil was not saturated, the DOC source pool could have changed as Hood (2006) identified that a decrease in DOC and aromaticity later in the storm event, is associated with water from deeper mineral soils on the hill slopes. Although in both the May and December 2005 events DOC exhaustion could have occurred, which will be easier to identify through the analysis of the second storm event that occurred within May and December 2005.

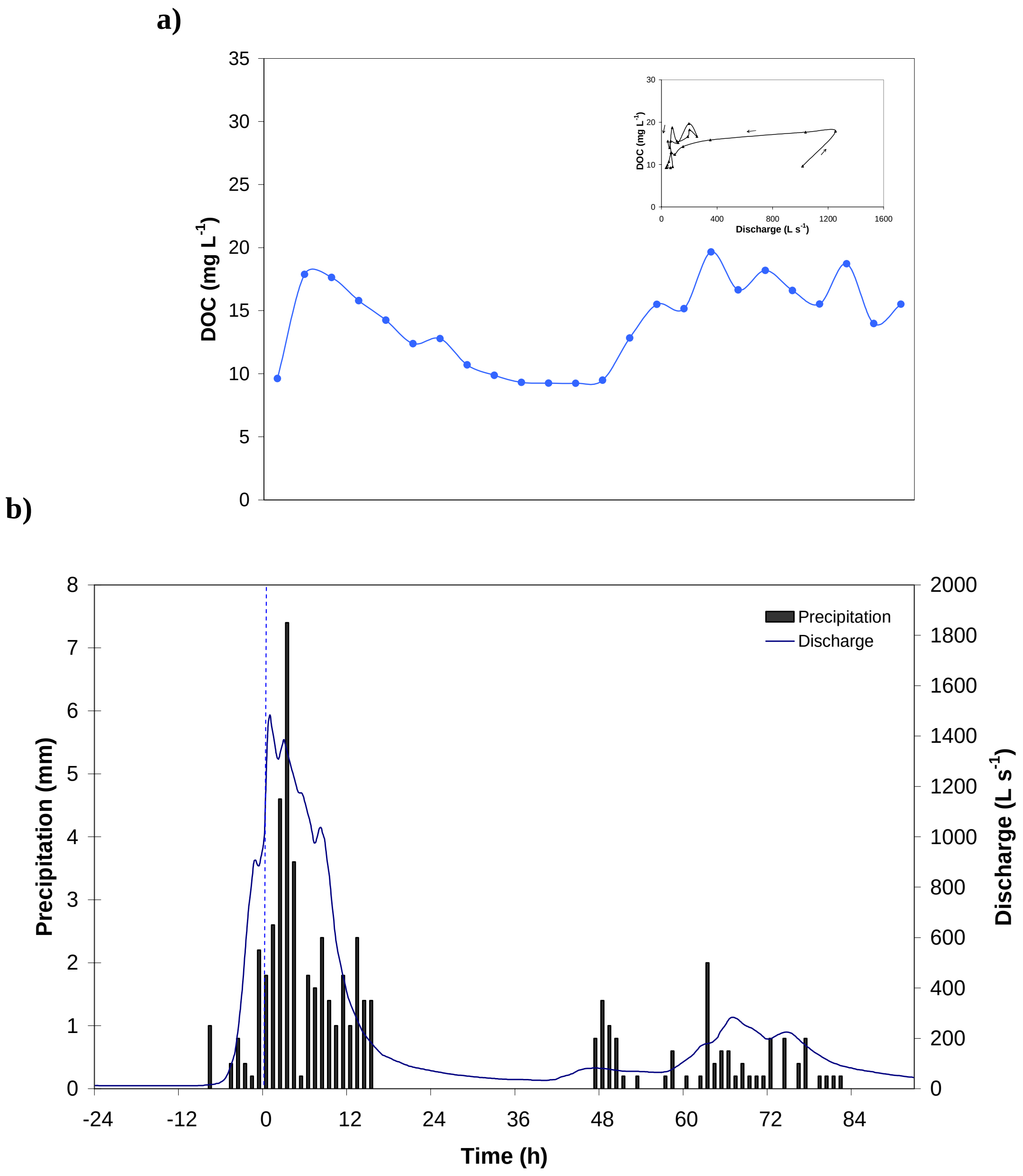


Figure 42: Measurements at the Duchray catchment of a) Dissolved organic carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals between 11.15 am on the 25h May and 07.15 am on the 29th May 2005, inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}), and b) Discharge (L s^{-1}) and precipitation (mm) measurements taken at 15 minute and 1 hour intervals respectively between 11.15 am on the 24h May and 07.15 am on the 29th May 2005. The dashed line illustrates when DOC sampling began.

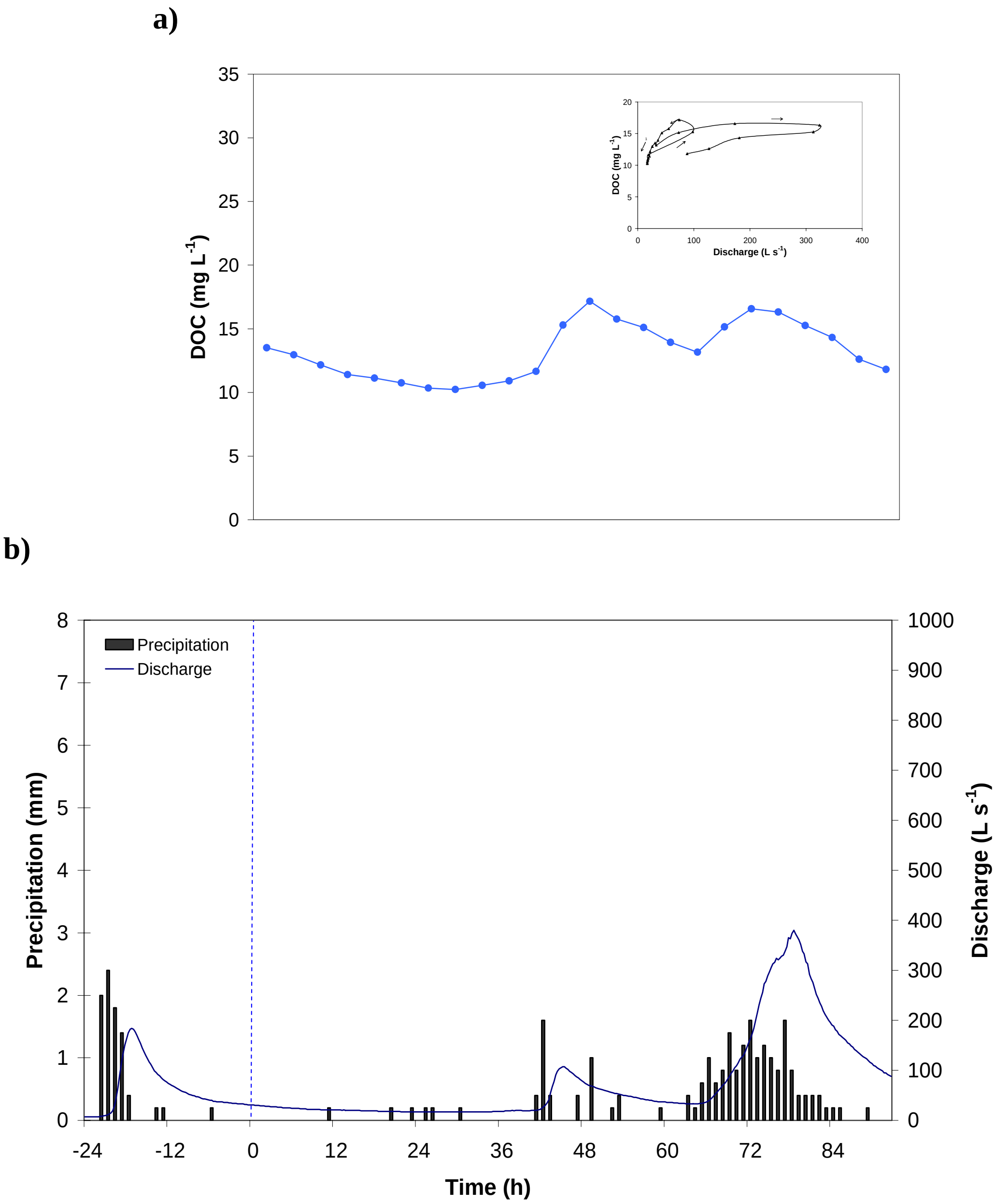


Figure 43: Measurements at the Duchray catchment of a) Dissolved organic carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals between 11.15 am on the 19th December and 7.15 am on the 23rd December 2005, inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}), and b) Discharge (L s^{-1}) and precipitation (mm) measurements taken at 15 minute and 1 hour intervals respectively between 11.15 am on the 18th December and 7.15 am on the 23rd December 2005. The dashed line illustrates when DOC sampling began.

The second hydrograph measured in the May and December 2005 events, followed wet antecedent conditions. When the second hydrograph was compared to the first in the sampling event a higher discharge peak (380 L s^{-1}) was measured in late December 2005, but a lower discharge peak was measured in May 2005 (283 L s^{-1}). Although the magnitudes of the storm events were different, during the second storm hydrograph in both events, DOC concentrations displayed clockwise hysteresis. Clockwise hysteresis during high intensity storm events has also previously been previously identified by Soulsby (1995), in an acidic afforested catchment in the Welsh uplands. In the December 2005 event, the sample taken two hours prior to the peak had a DOC concentration of 16.32 mg L^{-1}, and two hours after the peak concentrations were still high, but had reduced to 15.26 mg L^{-1}, at discharges of 324 L s^{-1} and 313 L s^{-1} respectively. In the May 2005 event the DOC concentration decreased from 19.66 mg L^{-1} two hours prior to the peak, to 16.65 mg L^{-1} two hours after the peak, at discharges of 197 L s^{-1} and 255 L s^{-1} respectively. It was also observed that when DOC concentrations were compared between the first and second hydrograph, that DOC concentrations had decreased slightly in the December, but increased in May.

During both May and December 2005, there was a gap between the two storm hydrographs sampled, which was longer during May 2005. During the gap, there was limited precipitation and a reduction in DOC concentration. It is suggested that following this gap, the groundwater level had decreased and water was no longer moving via sub-surface throughflow, where higher DOC concentrations are measured. However, when precipitation fell the depth of the groundwater increased in the soil and the flowpaths changed more rapidly to sub-surface throughflow than during the previous event, therefore producing high DOC concentrations on the rising limb of both storm hydrographs. Following the discharge peak, the soil may have become saturated and overland flow may occur, thus reducing DOC concentrations measured within the stream. This could explain why lower DOC concentrations were measured during the second hydrograph in the late December event although the discharges were greater than in the May 2005 event, as the change to overland flow could have been more rapid as the soil was more recently wet. However, it is suggested that the reduction in DOC observed after the second hydrographs, is due to exhaustion of DOC. This may have occurred specifically during the December 2005 event, because of reduced production and therefore availability of DOC during the winter months. However, this does not seem to be the case for the May event as concentrations of DOC remained high, even though the previous storm hydrograph was of great magnitude. It was also observed that after the second storm hydrograph in the May 2005 event, further inputs of precipitation produced a further increase in discharge and DOC concentration, and the concentrations were greater than were measured on the falling limb of the previous hydrograph.

During the August 2005 event (Figure 44) a similar pattern was observed to the May and December 2005 events, although both storm hydrographs measured followed wet antecedent conditions within the catchment. During the initial small hydrograph with a peak discharge of 57 L s^{-1}, a large increase in DOC concentration from 22.07 mg L^{-1} to 32.04 mg L^{-1} was measured at discharges of 9 L s^{-1} on the rising limb and 50 L s^{-1} on the falling limb. During the second storm hydrograph, which immediately followed the first, DOC exhibited clockwise hysteresis, decreasing from 31.94 mg L^{-1} four hours prior to the peak, to 28.7 mg L^{-1} 15 minutes after the peak, at discharges of 93 L s^{-1} and 977 L s^{-1} respectively. It would perhaps be expected that clockwise hysteresis would occur during the initial storm hydrograph as the soil was already wet as observed during May and December 2005, however it is suggested that greater availability of DOC during the summer and the low magnitude of the initial small event produced the anti-clockwise hysteresis during the initial event and the clockwise hysteresis during the second event when perhaps some DOC exhaustion was occurring.

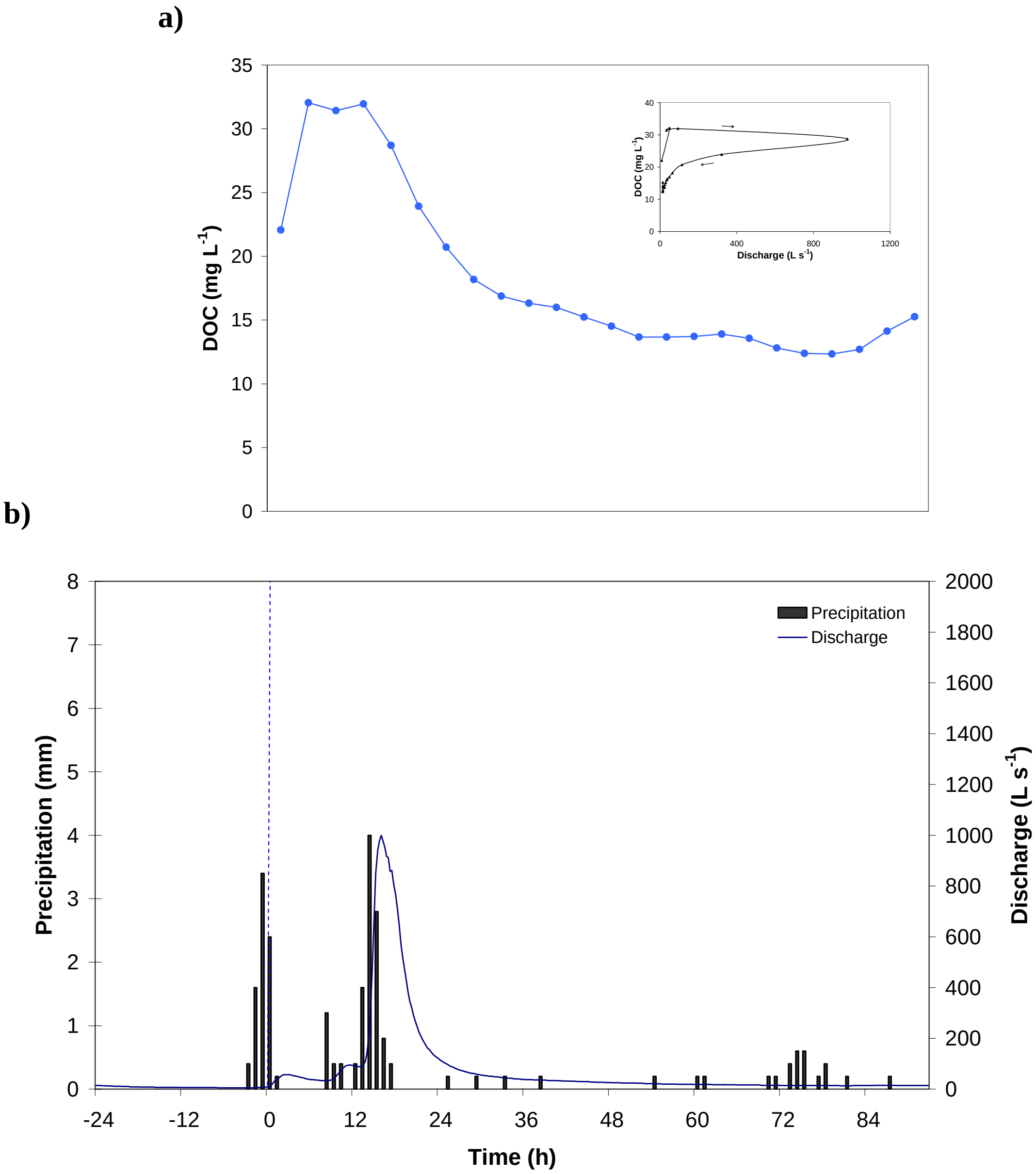


Figure 44: Measurements at the Duchray catchment of a) Dissolved organic carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals between 11.15 am on the 23rd August and 07.15 am on the 27th August 2005, inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}), and b) Discharge (L s^{-1}) and precipitation (mm) measurements taken at 15 minute and 1 hour intervals respectively between 11.15 am on the 22nd August and 07.15 am on the 27th August 2005. The dashed line illustrates when DOC sampling began.

5.3.3 Seasonal variations in DOC concentrations in the Duchray catchment

Seasonal variations in dissolved organic carbon (DOC) concentrations have been recognized in deciduous forests during the autumn when leaf fall occurs, when leachate becomes enriched with DOC (Hongve, 1999). However, as the Duchray is a coniferous forest catchment and needle fall occurs throughout the year, then it is thought that the leachate produced and its DOC concentration is governed by temperature (Hongve, 1999). The season is therefore potentially an important factor, in the concentrations of DOC that are being produced, and are available for export to the stream and seasonal differences in DOC concentrations have been found in the majority of studies (Grieve, 1994; Boissier and Fontvieille, 1995; Bernal *et al.*, 2002;) but not all, David *et al.* (1992) concluded that changes in discharge was more important

5.3.4 Seasonality of the DOC/discharge relationship

To examine the seasonal variation in the data collected, all dissolved organic carbon (DOC) concentrations, corresponding discharges and continuous discharge data were divided into seasons according to previous research (Wilby, 2001; Tank *et al.*, 2005; Pauling and Paeth, 2007), where each season encompasses three months of data and were thus divided into spring (March-May), summer (June-August), autumn (September-November) and winter (December-February), a summary of the data is shown in Table 10. This shows that overall a large range of DOC concentrations was measured within the Duchray catchment (3.93-46.35 mg L^{-1}), but the concentrations of DOC within the individual seasons varied. It can be observed that mean and median DOC concentrations were at their lowest during the winter, increased through the spring and autumn, and were highest during the summer. The DOC concentrations measured during the summer and autumn also covered a larger range, than during the spring and winter. The range of the instantaneous discharges, which correspond to the samples taken for DOC analysis, covered a wide range of discharges (2-1253 L s^{-1}), but did not cover the full range of discharges that were measured throughout the sampling period (2-2025 L s^{-1}). When examining the instantaneous discharges during the seasons, it can be identified that the magnitude of the discharges change during the seasons, with the smallest mean and median discharges measured during the summer, increasing slightly in the winter, further in the autumn and were greatest in the spring. When the instantaneous discharges, were compared with the overall discharge seasonal values, differences can be observed during the spring where higher instantaneous mean and median discharges were measured, and during the winter which had lower instantaneous mean and median discharges, because of the limited range of discharges that were sampled during the winter.

Table 10: The mean, median and ranges of dissolved organic carbon (DOC) and the corresponding instantaneous discharges and all discharges (taken at 15 minute intervals) measured at the Loch Ard Duchray Catchment during spring, summer, autumn and winter and the overall mean, median and range.

Season	Descriptive statistics	DOC (mg L^{-1})	Instantaneous discharges	All discharges (L s^{-1})
Spring	Mean	10.43	133.9	49.8
	Median	9.48	43.5	19
	Range	3.93 -19.66	7 - 1253	4-1484
		(n=72)	(n=72)	(n=8833)
Summer	Mean	18.83	36.1	26.36
	Median	16.53	9	6
	Range	8.97 - 46.35	2 - 977	2-2025
		(n=88)	(n=88)	(n=17629)
Autumn	Mean	17.81	52.80	58.27
	Median	16.09	26	25
	Range	10.41 - 44.43	3 - 830	3 – 1298
		(n= 101)	(n= 101)	(n=12798)
Winter	Mean	9.05	36.46	77.26
	Median	7.74	20	32
	Range	4.14 -17.16	10-324	6 – 1677
		(n=94)	(n=94)	(n=13826)
Total	Mean	14.25	60.79	51.2
	Median	12.96	19	18
	Range	3.93 – 46.35	2-1253	2-2025
		(n=355)	(n=355)	(n=53086)

To examine the seasonal patterns in the relationship between DOC concentrations and the log of discharge (log Q), the Pearson's product moment correlation coefficient was calculated for each season. The strongest correlation between DOC and log Q was identified during the winter (r =0.756, df =92, P<0.01) and spring (r =0.594, df =70, P<0.01) where 57 and 35% of the variation in DOC and log Q was in common. The correlation weakened during the summer (r =0.465, df =86, P<0.01) and autumn (r =0.436, df =99, P<0.01) as the variables had only 22 and 19% of their variation in common. The strength of the relationships can be observed in the scatterplots shown in Figure 45 and in the regression equations in Table 11. Similar slopes of the regression line are seen in the summer and autumn, although the slope was slightly steeper in the summer and also had the highest intercept. Considerable scatter is also seen around both the autumn and summer regression lines suggesting that different DOC/discharge relationships exist during the summer and autumn.

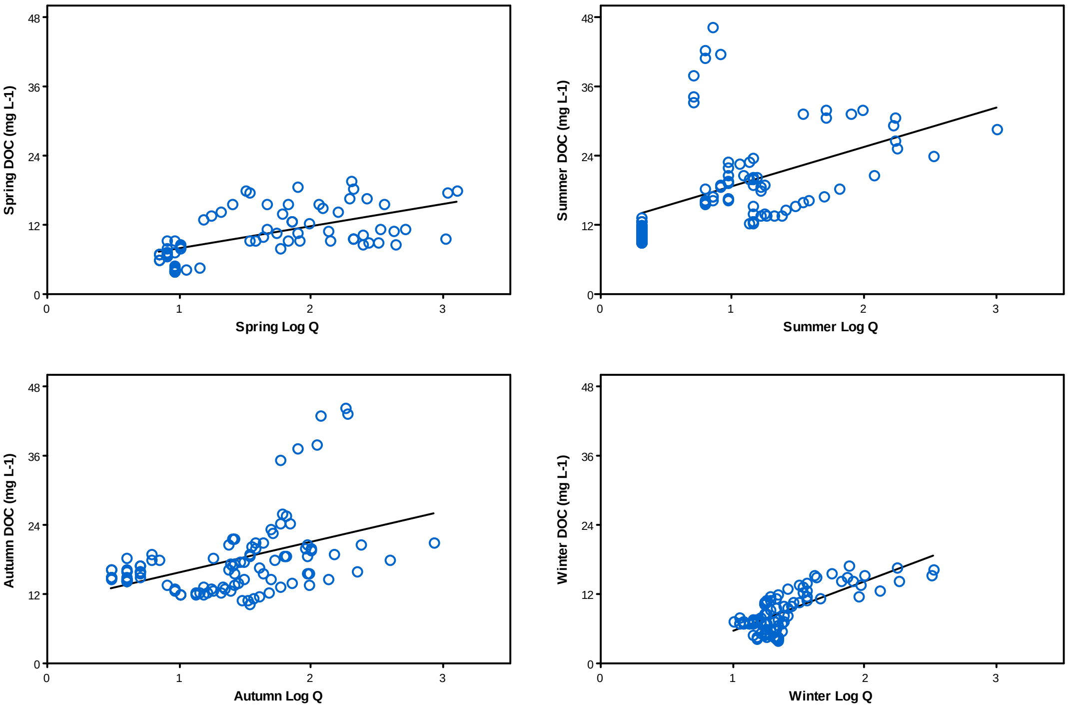


Figure 45: Scatterplots of dissolved organic carbon (DOC) plotted against the log of discharge (Q) produced from results taken from the Duchray catchment, separated by season (spring (R^2=0.35), summer (R^2=0.22), autumn (R^2=0.19) and winter (R^2=0.57)).

During the spring and winter there is reduced scatter which produces the stronger relationship identified. The slope is reduced during the spring because of the low concentrations measured during all discharges. However, the steepest slope was measured during the winter, which is perhaps due to the mainly low DOC concentrations measured at low discharge and the negative intercept. Unlike the Ochil Hills catchment where the seasonal relationship weakened the overall relationship, in the Duchray, the strength of the DOC /discharge relationship improves during all seasons.

Table 11: Summary table of seasonal and overall regressions of DOC (mg L^{-1}) on discharge (Q), produced from data collected from the Duchray catchment between 2004 and 2006.

Season	Seasonal regression equations (coefficients ± standard error)	R^2
Spring	$DOC = 4.27 + 3.77 \text{ Log } Q$ $\pm 1.08 \quad \pm 0.61$	0.35
Summer	$DOC = 12.1 + 6.73 \text{ Log } Q$ $\pm 1.61 \quad \pm 1.38$	0.22
Autumn	$DOC = 10.5 + 5.31 \text{ Log } Q$ $\pm 1.64 \quad \pm 1.11$	0.19
Winter	$DOC = - 2.95 + 8.58 \text{ Log } Q$ $\pm 1.11 \quad \pm 0.78$	0.57
Overall	$DOC = 10.4 + 2.84 \text{ Log } Q$ $\pm 0.99 \quad \pm 0.68$	0.045

5.3.4.1 Summer (June – August)

It was during the summer months that the largest range of dissolved organic carbon (DOC) concentrations were measured, as well as both the highest mean and median concentrations and the steepest slope of the regression which suggested a large store of DOC was available within the catchment during the summer. However, a weak correlation was found between DOC and the log of discharge during the summer (R^2 =0.22) and it was observed within the scatterplot (Figure 45) illustrating the relationship between summer DOC and log Q, that different relationships existed. These different relationships are due to samples taken during events in August 2004 and 2005, when a larger range of concentrations were measured in August 2004 (33.26 - 46.35) than August 2005 (12.34 - 32.4 mg L^{-1}); the high concentrations measured during August 2004 were also taken during low discharges (5 - 8 L s^{-1}), but the August 2005 samples were taken at much greater discharges (9 - 977 L s^{-1}). The influence of the high concentrations measured during August 2004 at low discharges can be observed if the relationship between DOC and log Q is compared between summer 2004 and 2005, as shown in Figure 46. Where the correlation between DOC and log Q was not significant during summer 2004 (r = -0.284, df =19, P=0.212), but it was during summer 2005 (r = 0.726, df= 64, P<0.01) and DOC and log Q had 53% of their variation in common. The difference between the slope of the summer regression lines, shown in Figure 46, is primarily due to high DOC concentrations measured during the August 2004 event, and because of the increased number of samples collected over a great range of discharges during summer 2005.

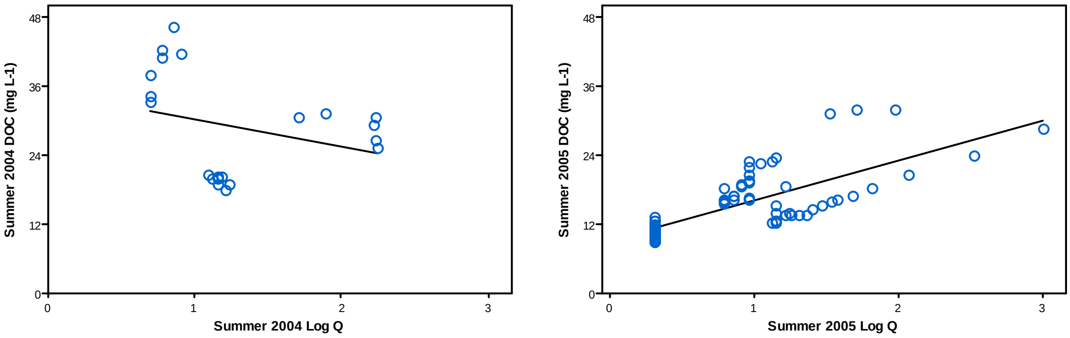


Figure 46: Scatterplots showing the relationship between dissolved organic carbon (DOC) and the log of discharge during summer 2004 (R^2=0.08) and summer 2005 (R^2=0.53).

This however shows that high DOC concentrations are available during both high and low discharges. Previous research has identified that available concentrations of DOC are typically higher during the summer months as observed in the Duchray due to increased biological activity (Cole *et al*., 2002). Rainfall has also been identified to promote an increase in biological activity (Boissier and Fontvieille, 1995), and thus high concentrations of DOC are typically measured during summer storm events (Grieve, 1994; Bernal *et al*., 2002). This is supported by the samples that were collected in August 2005 (Figure 44) high concentrations of DOC were measured during this storm event and the highest DOC concentration (32.04 mg L^{-1}) was measured during the first small storm hydrograph with a peak discharge of only 57 L s^{-1}. Previous research (Bernal *et al*., 2002) has identified that during the summer months, organic matter accumulates both in the stream bed and the riparian zone and it is this organic matter that is initially leached during storm events producing the high concentrations of DOC that were measured. The second storm hydrograph in the August event was of much greater magnitude than the first peaking at 1000 L s^{-1}. The DOC concentrations during this hydrograph were only slightly lower than the first, suggesting high DOC concentrations were still available within the catchment.

5.3.4.2 Autumn (September – November)

A good correlation between dissolved organic carbon (DOC) and the log of discharge was found for the autumn months (R^2 = 0.47). The mean, median and range of DOC concentrations, were only lower than those measured during the summer and a similar regression slope was measured to the summer, suggesting that stores of DOC within the catchment are still high during the autumn. However, the concentrations measured during the autumn were found to decrease as the autumn progressed. High concentrations of DOC were measured during early September 2004 (35.33-44.43 mg L^{-1}) during discharges ranging from 58 -183 L s^{-1}, yet in late September 2005 a much lower range of concentrations were measured (10.41-20.85 mg L^{-1}) during discharges ranging from 29 -833L s^{-1}. However, high concentrations of DOC continued to be available in the catchment as autumn progressed, as in the October 2005 event (Figure

40), a good range of DOC concentrations were measured (13.3-26 mg L^{-1}) although the storm hydrograph was only small with a discharge peak of 67 L s^{-1} and this range of values, is similar to those measured during the initial, and comparative storm hydrograph in August 2005 (Figure 44). During November 2004 (Figure 36), the concentrations had decreased, (14.18-19.03 mg L^{-1}) when compared to the other events sampled during the autumn period, however the discharges measured were low (3-7 L s^{-1}).

5.3.4.3 Winter (December – February)

A good correlation between dissolved organic carbon (DOC) and the log of discharge was found during the winter ($R^{2=}$ 0.57) and the lowest mean and median and range of DOC concentrations were measured, although the slope of the DOC/discharge regression was the greatest, however the intercept was the lowest and negative. This reduction in DOC concentrations during the winter can be observed in both the early and late December 2005 events (Figure 39 and Figure 43), where concentrations ranged from 7.38 to 15.29 mg L^{-1} in early December, and 10.24 to 17.16 mg L^{-1} in late December. If these events are compared to the October 2005 event, it can be observed that much lower ranges of DOC concentrations were measured during December 2005, although similar discharges were measured during October and the early December event and higher discharges were measured during the late December 2005 event. The increase in DOC concentration during the second December event suggests that there is still DOC available within the catchment, however the reduction in concentration when compared to the October event indicates that as has been identified previously (Grieve, 1984b), microbial activity decreases during the winter, depleting the available DOC concentration within the catchment, which will further deplete as the winter progresses.

5.3.4.4 Spring (March – May)

A weak correlation was identified between dissolved organic carbon (DOC) concentration and discharge during the spring (R^2= 0.35). The mean, median and range of DOC concentrations, measured during the spring were greater than the winter, but less than the summer and autumn, which was shown by the slope of the DOC/discharge regression which was less than the summer and autumn. During the initial event sampled during the spring in March 2005 (Figure 38), the range of DOC concentrations measured in the catchment (4.03 to 11.21 mg L-1), were lower than measured during the winter samples taken in late December 2005 (Figure 43) (10.24 to 17.16 mg L^{-1}), although the range of discharges were similar. This indicates that lower DOC concentrations were available for movement at the start of spring during the March event, as during this event, although the catchment was initially dry, a large quantity of precipitation (51.4 mm) fell during the sampling period, but the largest DOC concentration measured was only 11.21 mg L^{-1} suggesting limited availability of DOC. As temperatures begin to rise and microbial activity again increases, higher DOC concentrations are available for movement from the catchment to the stream. High DOC concentrations were observed in May 2005 (Figure 42), during both the first large storm hydrograph and the second smaller storm hydrograph, where concentrations were higher, suggesting that there is a large DOC pool available for movement to the stream. Previous research also found that DOC concentrations during the spring were lower than during the summer, even if the same magnitude of storms and antecedent conditions exist (Bernal *et al*., 2002).

5.4 Summary

An examination of the results from the Duchray catchment revealed the poor relationship that exists between dissolved organic carbon (DOC) and the log of discharge (R^2 =0.048). It was further identified that although DOC concentrations increased during high discharges, high DOC concentrations were also measured during periods of low discharges, indicating that a combination of factors were contributing to the final concentration of DOC measured within the stream. Potential controls of DOC concentration were identified through an examination of the storm events sampled. During storm events that followed dry antecedent conditions the dominant hysteresis of DOC was anti-clockwise. It is suggested that the source of the low DOC concentrations on the rising limb of the hydrographs is groundwater displaced by the falling precipitation. As the storm progressed higher DOC concentrations were measured on the falling limb of the hydrograph as the precipitation moving through the upper soil horizons to the groundwater was enriched with DOC. The flowpaths changed during storm events that followed wet antecedent conditions as clockwise hysteresis of DOC was seen to dominate. Initial high DOC concentrations were measured, because the soil was already wet and the precipitation was moving through the organic shallow subsurface soils where concentrations of DOC are high. The reduction in DOC on the falling limb is potentially due to exhaustion of DOC or due to saturation of the soil and overland flow occurring. The examination of the storm events highlighted the importance of the hydrological flowpaths followed to the stream in controlling concentrations of DOC, which is in term controlled by the antecedent conditions within the catchment prior to samples were taken, the amount of precipitation that fell on the catchment and the intensity of the precipitation. This was further confirmed by the changing flowpaths that occurred during storm events following wet antecedent conditions, the initial storm hydrograph exhibited anti-clockwise hysteresis, but the second storm hydrograph exhibited clockwise hysteresis.

The hydrology of the catchment could not explain all the variance in DOC concentrations, and the importance of season was confirmed when the data was sub-divided into season as the relationship between DOC and the log of discharge during the spring ($R^2 = 0.35$), summer ($R^2 =0.22$) autumn ($R^2 = 0.19$) and winter ($R^2 = 0.57$) were stronger than the overall relationship ($R^2 = 0.048$). It was also identified through an examination of the regression relationships, that in general greater concentrations of DOC were measured during the summer and autumn at a given discharge. Limited exhaustion in DOC was also observed during the summer and autumn suggesting that larger stores of DOC are available within the catchment than during the winter and spring when exhaustion was observed.

Chapter 6 - Elrig Catchment

6.1 Introduction

The aim of chapter 6 is to describe and discuss the results from the Elrig catchment within the Loch Ard site, focussing on the relationship between dissolved organic carbon (DOC) concentrations and discharge. The specific aim is to establish potential controls of dissolved organic carbon concentrations fluxes within the Elrig catchments, objective 1 of this research and to test the hypothesis that temperature and the hydrology of the catchment are the main drivers of short term changes in DOC concentrations in the Elrig stream. The results from the Elrig catchment will also be compared with the results from the Duchray catchment, to identify if trends in the DOC/discharge relationship are similar in both catchments. The DOC results discussed in this chapter are from samples taken from the Elrig catchment between the 10th June 2004 and 27th January 2006; a total of fourteen sample sets were taken at four hour intervals. The number of samples collected in the Elrig catchment were limited by technical problems, however, the DOC concentrations measured (6.29-39.73 mg L^{-1}) were taken during almost the full range of discharges measured in the Elrig catchment (4-2695 L s^{-1}). The total number of samples used within the analysis of the results was 248.

6.2 Overview of results from the Elrig catchment

Figure 47 shows all precipitation, discharge and dissolved organic carbon (DOC) results collected for the Elrig catchment. Figure 47 shows that a good relationship exists between precipitation and discharge. This would be expected, but as with the Duchray (section 5.2) there may be inconsistencies between the two data sets.

The DOC concentrations show pronounced seasonal variations; the highest concentrations were measured during the late spring (June) and summer (August and September) 2004, although low concentrations were measured in July 2004. A similar trend was identified within the Duchray catchment. Another trend identified in both catchments, was that higher concentrations were measured in 2004 than 2005, the difference was however less pronounced in the Elrig catchment. The same seasonal trends were observed in both catchments, the lowest DOC concentrations were measured during the winter (December and February) and early spring (March), and intermediate concentrations were measured in the spring (April and May). This suggests that, as with the Duchray catchment, season is an important control of DOC concentrations in the stream.

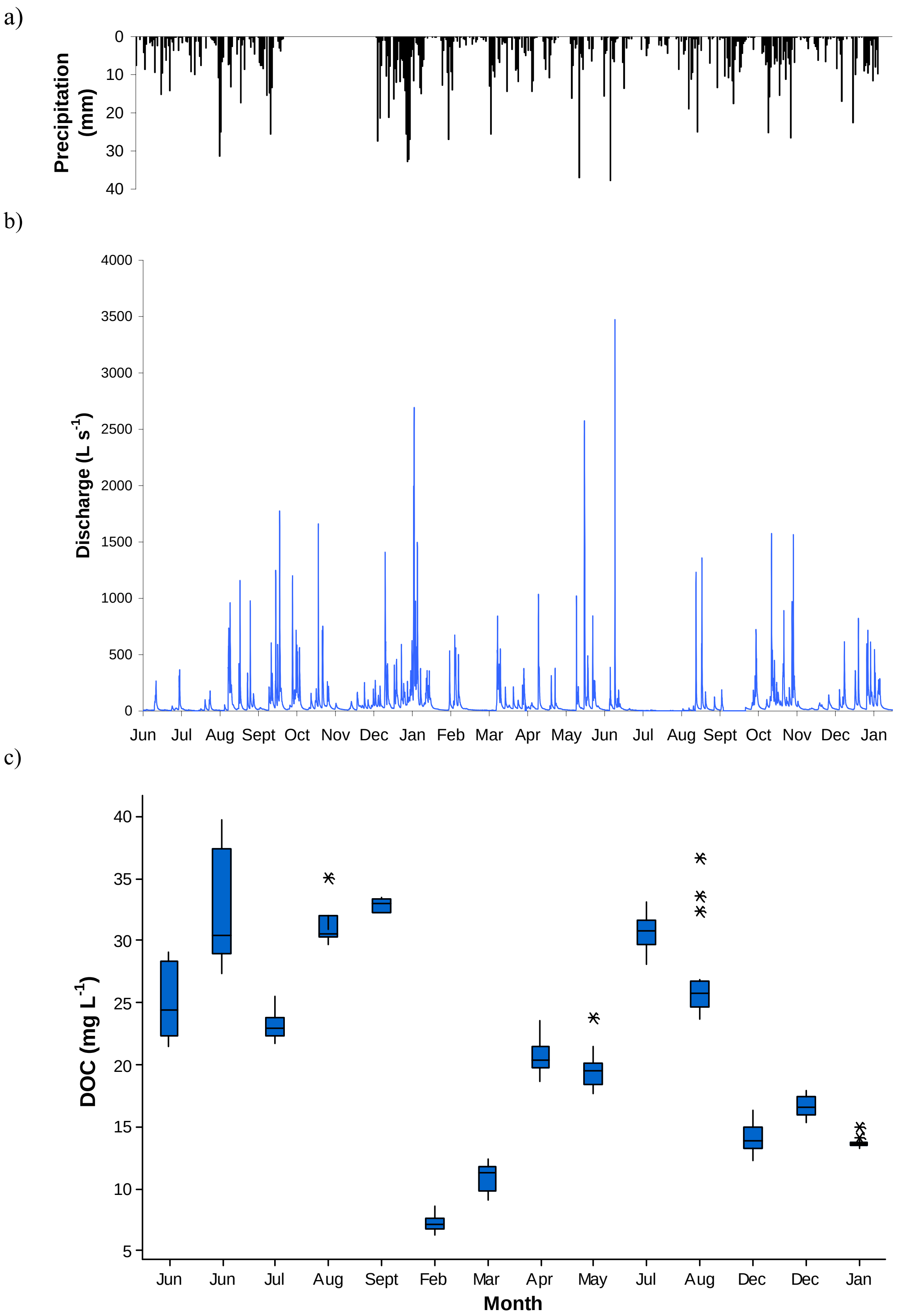


Figure 47: All measurements taken at the Elrig catchment of a) Daily precipitation (mm) (data missing between 29th September and 12th December 2004), b) Average hourly discharge (L s^{-1}) (data missing between the 15th September and 3rd October 2005) and c) Boxplots showing 14 sample sets of dissolved organic carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals, between June 2004 and January 2006.

6.3 Comparison of results between the Duchray and Elrig catchment

Potentially important drivers of DOC concentration within the Duchray catchment were identified in chapter 5 and include the amount of precipitation falling on the catchment, the antecedent precipitation and season. To identify if the same controls are important in the Elrig catchment, then the overall DOC/discharge relationship will be compared and how this relationship changes during baseflow and storm events will be examined.

6.3.1 DOC/discharge relationship

The correlation between DOC and the log of discharge (log Q) was not significant (r = -0.066 df = 246, P=0.301) and the relationship is shown in Figure 48. This contrasts with the DOC/log Q correlation in the Duchray catchment which was weak (R^2 = 0.045) but still significant (P<0.01). The Elrig catchment contains an area of wetland and previous research in forested sites that contain an area of wetland have also found no significant relationship between DOC and discharge (Hinton *et al.*, 1997).

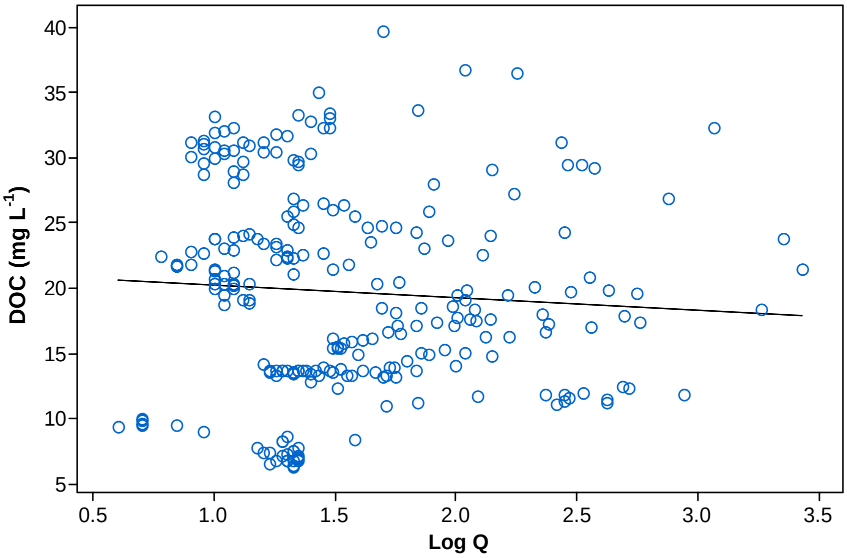


Figure 48: Scatterplot showing the relationship between dissolved organic carbon (DOC) and the log of discharge (log Q), in the Elrig catchment between the 10th June 2004 and the 27th January 2006.

6.3.2 DOC relationship with low discharge

During periods of low discharge within the catchment, the principal source of dissolved organic carbon (DOC) within the Duchray catchment was the groundwater (e.g. Soulsby, 1995). To identify how baseflow DOC concentrations, differed between the two catchments, a series of sampling events were analysed. Unfortunately during many of the base flow sample sets taken from the Duchray, samples were not taken in the Elrig. However, in the March 2005 event when the antecedent conditions were dry, a series of samples taken prior to any precipitation showed that DOC concentrations measured in the Duchray (3.93-4.87 mg L^{-1}), were much lower than in the Elrig (9.36-9.93 mg L^{-1}), although the baseflow discharges were slightly higher in the Duchray (9-10 L s^{-1}) than in the Elrig (4-5 L s^{-1}). Similar differences in DOC concentration can be observed in the final sample taken after the storm event during the early December 2005 event when the stream had returned to baseflow conditions. The DOC concentration measured in the Elrig catchment (12.78 mg L^{-1}) at a discharge of 25 L s^{-1} was greater than measured in the Duchray catchment (7.38 mg L^{-1}) at a lower discharge of 14 L s^{-1}. The greatest difference in DOC concentration, between the catchments was observed in the final samples taken during the August 2005 event when the streams had returned to baseflow conditions after the storm event. The DOC concentration in the Elrig catchment was 26.85 mg L^{-1}, at a discharge of 21 L s^{-1}, but the concentration in the Duchray was much lower (15.26 mg L^{-1}) although the discharge was also lower in the Duchray (14 L s^{-1}). It can therefore be concluded that consistently greater baseflow DOC concentrations are produced in the Elrig catchment; this is because of the different topography and the soil types within the catchments. The Duchray has sleeper slopes than the Elrig catchments, therefore less organic matter accumulates and has a greater proportion of mineral soil, therefore more of the DOC produced will be adsorbed by Fe within the B horizon (McDowell and Wood, 1984; Jardine *et al.*, 1989; Moore *et al.*, 1992). In the Elrig the soil is more organic; therefore more DOC is available for movement to the stream.

6.3.3 DOC/discharge relationship during storm events following dry antecedent conditions

When dissolved organic carbon (DOC) was plotted against discharge during storm events following dry antecedent conditions (Figure 49) in the Elrig catchment, it can be observed that in all the plots the DOC concentration displayed anti-clockwise hysteresis, except during March 2005, where similar values were measured on the falling and rising limb of the storm hydrograph. Anti-clockwise hysteresis also dominated in the Duchray catchment, and similar values were also measured on the rising and falling limb of the March 2005 event. Clockwise hysteresis was not observed in the Elrig catchment; the October 2005 event which showed clockwise hysteresis in the Duchray, was not sampled in the Elrig. The dominance of anti-clockwise hysteresis following dry antecedent conditions in both catchments, suggests that the flowpaths identified in the Duchray catchment (section 5.3.2.1), are also controlling DOC movement in the Elrig. Where the initial low DOC concentrations on the rising limb of the storm hydrograph result from precipitation displacing the groundwater, and as the flow path changes to sub-surface throughflow, where higher DOC concentrations are available, DOC concentrations increase on the falling limb of the hydrograph (Evans *et al.,* 1999). The similar DOC concentrations measured on the rising and falling limb of the storm event in March 2005 suggests that there are limited stores of DOC available in both catchments at this time of year.

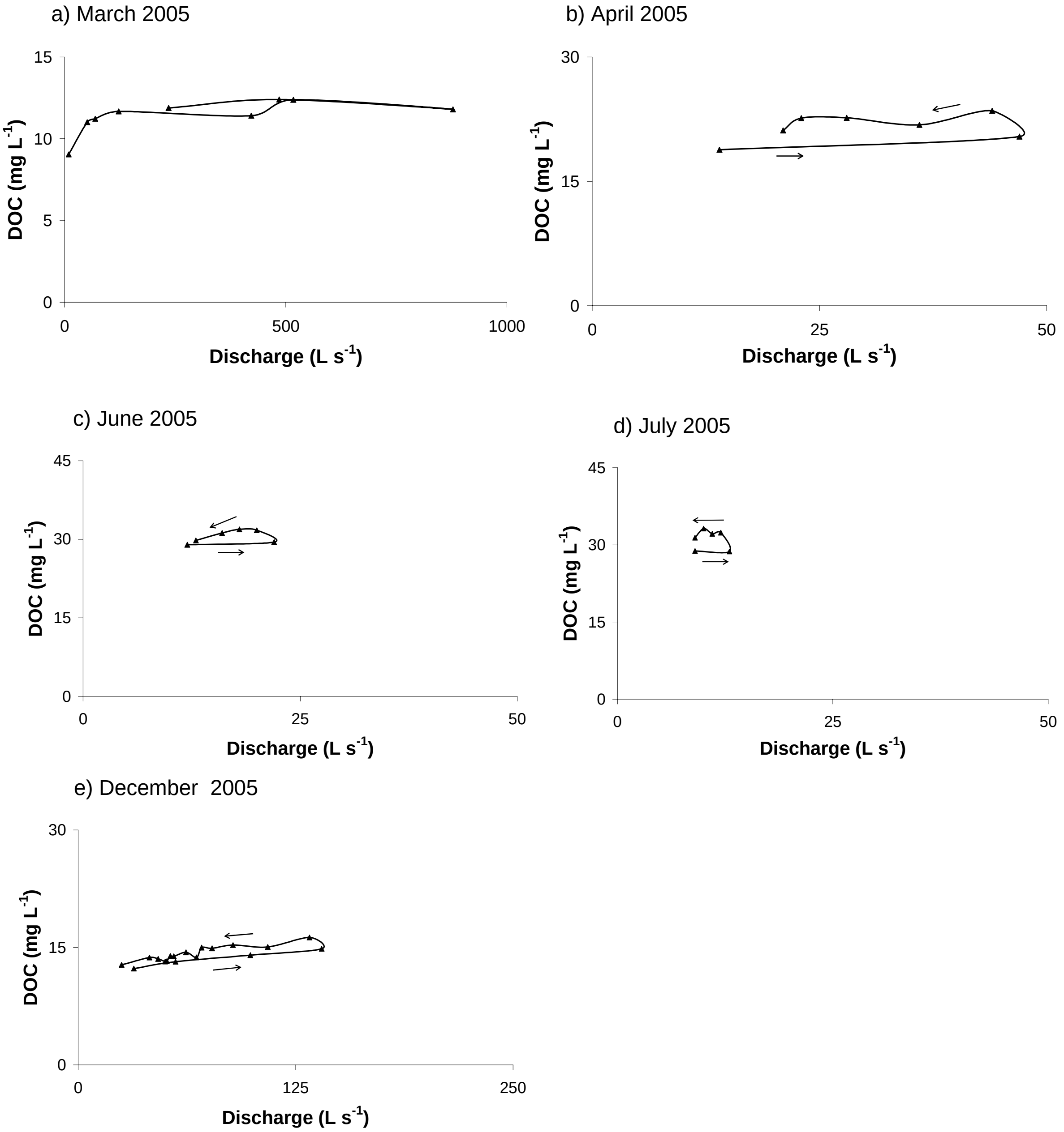


Figure 49: Hysteresis loops of dissolved organic carbon (DOC) plotted against discharge, during storm events following dry antecedent conditions in the Elrig catchment.

Although anti-clockwise hysteresis was identified to be dominant in both catchments, when the storm events are compared differences between the catchments can be identified. During the early December 2005 event (Figure 50) in the Duchray catchment, similar DOC concentrations were measured on the rising (14.18 mg L^{-1}) and falling limb (13.51 and 14.2 mg L^{-1}) of the storm hydrograph (the sample taken following these samples is potentially erroneous as discussed in section 5.3.2.1), but anti-clockwise hysteresis was observed in the Elrig (Figure 50) where DOC concentrations increased from 14.83 mg L^{-1} on the rising limb to 16.27 mg L^{-1} on the falling limb. This suggests that higher DOC concentrations are more readily available for movement in the Duchray catchment, however the range of concentrations measured during this sampling event were greater in the Elrig (12.3- 16.7 mg L^{-1}) than the Duchray (7.38-15.29 mg L^{-1}) suggesting a larger store of DOC is available within the Elrig catchment. High DOC concentrations were also sustained longer after the hydrograph peak in the Elrig, as the final concentrations measured 3 days after the peak discharge, were 12.78 mg L^{-1} in the Elrig and 7.66 mg L^{-1} in the Duchray.

To determine if there is a larger DOC store within the Elrig catchment, then a high intensity storm event measured during March 2005 in both events (Figure 51) will be examined. During this large storm event, 51.4 mm of precipitation fell on the catchments over a three day period, producing five large discharge peaks which are labelled 1-5 in Figure 51. The range of DOC concentrations measured within the Elrig (8.42-12.4 mg L^{-1}) and Duchray catchments were similar (4.03-11.21 mg L^{-1}), although a greater range of discharges were measured in the Elrig (4-878 L s^{-1}) than the Duchray (9-611 L s^{-1}). However, although the DOC concentrations measured within the catchments were similar, how DOC concentrations changed during the storm event was not.

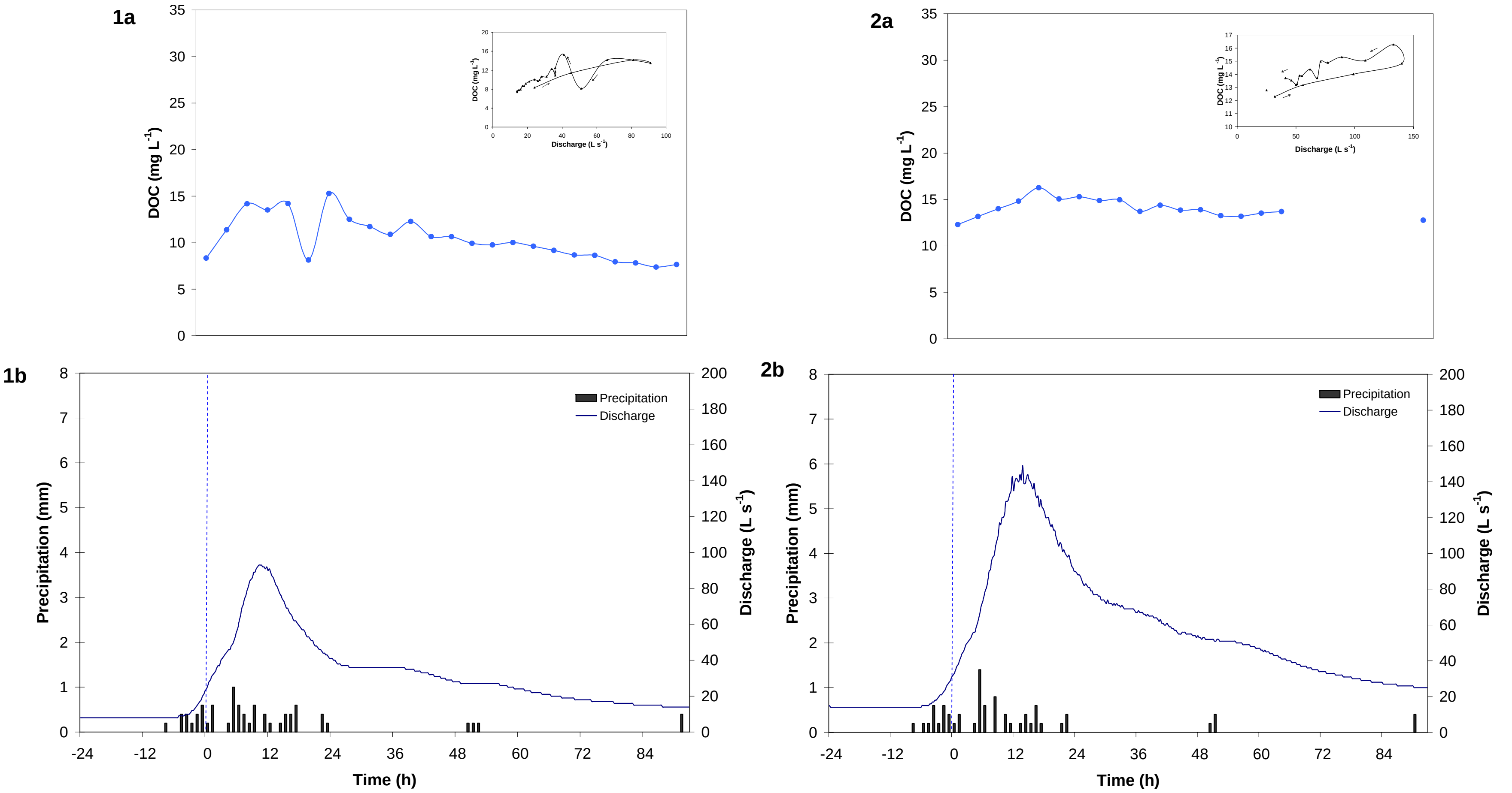


Figure 50: Measurements at the Duchray (1) and Elrig Catchment (2) of a) Dissolved organic carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals between 12.00 am on the 9th December and 9.30 am on the 13th December 2005 in the Duchray and between 12.30 pm on the 9th December and 08.30 am on the 13th December 2005 in the Elrig catchment (6 missing samples) , inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}), and b) Discharge (L s^{-1}) and precipitation (mm) taken at 15 minute and 1 hour intervals respectively, between 12.00 am on the 8th December and 9.30 am on the 13th December 2005 in the Duchray catchment and between 12.30 pm on the 8th December and 08.30 am on the 13thDecember 2005 in the Elrig catchment . The dashed line illustrates when DOC sampling began.

In the Duchray during an initial small storm hydrograph (not measured in the Elrig), DOC concentrations exhibited anti-clockwise hysteresis, measuring 7.89 mg L^{-1} at the peak discharge (58 L s^{-1}) and 11.27 mg L^{-1} on the falling limb, 4 hours later. The discharge continued to increase in the Elrig and during the first two large storm hydrographs (1-2) in both streams, the DOC concentrations were higher than the base flows, although a greater initial increase in DOC concentration was measured in the Duchray. During the first hydrograph (1) in the Elrig, where a peak discharge of 547 L s^{-1} was measured, DOC concentrations exhibited limited anti-clockwise hysteresis, where the concentration increased from 11.41 mg L^{-1} on the rising limb to 12.38 mg L^{-1} on the falling limb, at discharges of 422 and 517 L s^{-1}. During the first hydrograph (1) in the Duchray catchment, similar DOC concentrations were measured on the rising (10.98 mg L^{-1}) and falling limbs (11.03 and 11.31mg L^{-1}), at discharges of 132, 417 and 323 L s^{-1}. However, the discharge peak (430 L s^{-1}) was measured ~2.5 hours prior to the discharge peak in the Elrig, indicating a more rapid response to precipitation in the Duchray catchment, potentially due to that catchment's steeper slopes. During a second and larger storm hydrograph (2), which had discharge peaks of 878 L s^{-1} in the Elrig and 611 L s^{-1} in the Duchray, DOC concentrations changed as was observed in hydrograph (1). In the Elrig, DOC concentration increased from 11.8 mg L^{-1} at the discharge peak to 12.4 mg L^{-1} on the falling limb, and in the Duchray catchment, DOC concentrations again remained similar throughout the hydrograph, measuring 11.31 mg L^{-1} prior to the peak discharge, decreasing to 11.21 mg L^{-1} after the peak. The discharge peak in the Elrig catchment was again observed to lag ~2.5 hours behind the discharge peak in the Duchray. During the last three discharge peaks in the March event (3-5), concentrations remained high in the Elrig catchment, but showed limited variability (11.05-11.91 mg L^{-1}). However, in the Duchray catchment, DOC concentrations decreased further (8.68-9.53 mg L^{-1}). This suggests that either more exhaustion is occurring in the Duchray catchment or that due to the intensity and length of the storm event, overland flow is occurring in the Duchray catchment, due to its steeper slopes and therefore DOC concentrations are reduced.

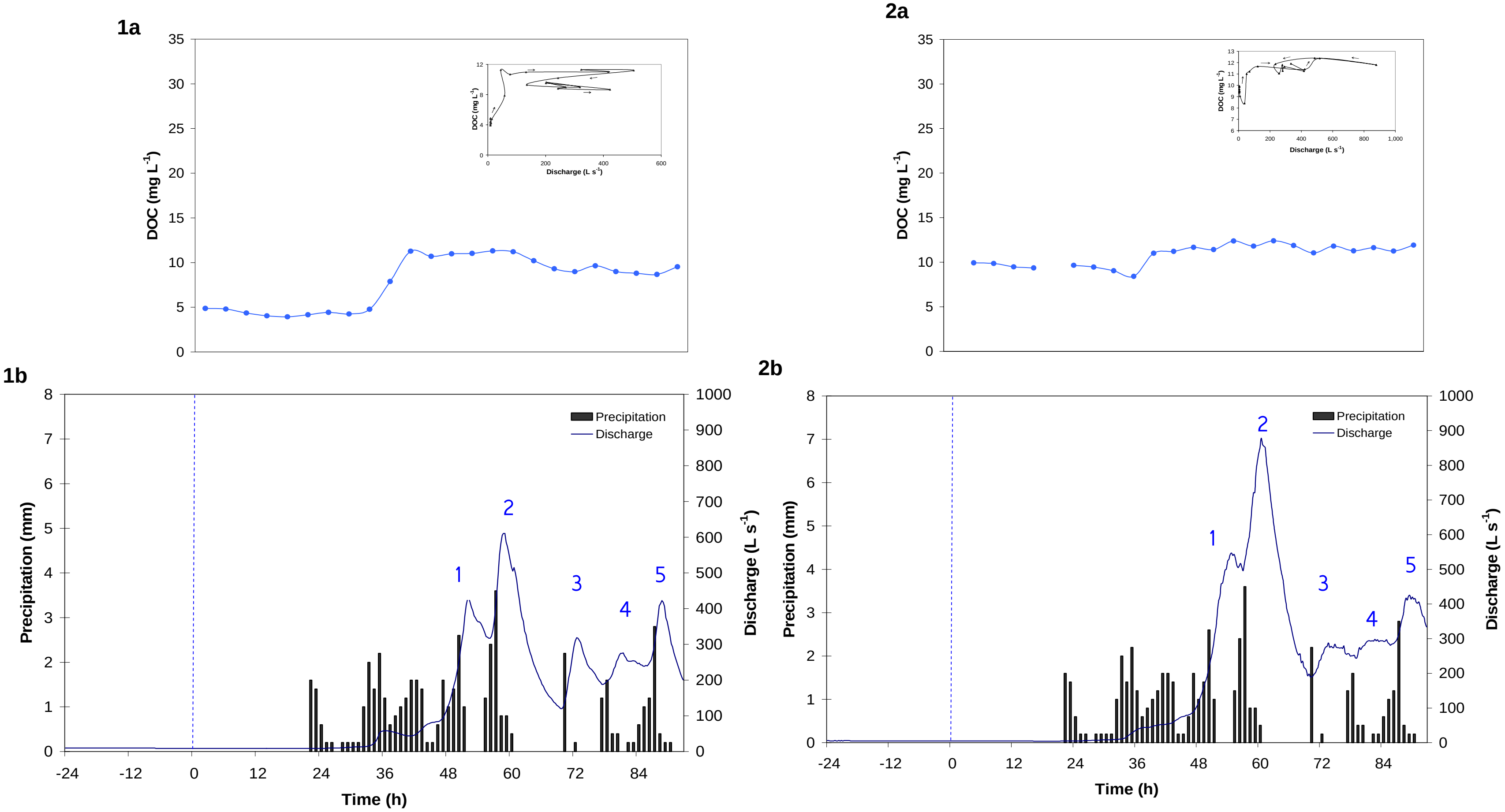


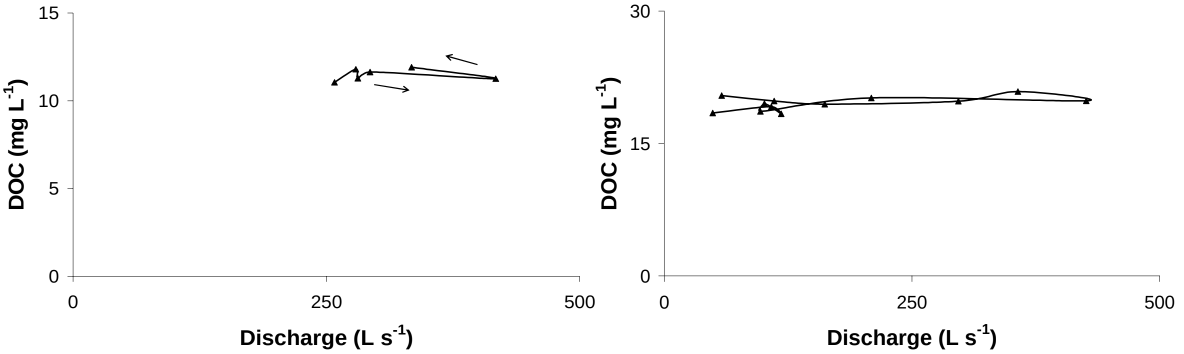
Figure 51: Measurements at the Duchray (1) and Elrig Catchment (2) of a) Dissolved organic carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals between 11.00 am on the 13th March and 07.00 am on the 17th March 2005 (two sample missing from the Elrig(2)), inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}), and b) Discharge (L s^{-1}) and precipitation (mm) taken at 15 minute and 1 hour intervals respectively, between 11.00 am on the 12th March and 07.00 am on the 17th March 2005. The dashed line illustrates when DOC sampling began and storm hydrographs are numbered 1-5.

6.3.4 DOC/discharge relationship during storm events following wet antecedent conditions

When dissolved organic carbon (DOC) was plotted against discharge during storm events following wet antecedent conditions (Figure 52), it can be observed that limited DOC hysteresis occurs in the Elrig catchment. No hysteresis occurred during the May 2005 event, anti-clockwise hysteresis was seen during March and December 2005, and clockwise hysteresis was seen in August and December 2005. However similar values were measured on the falling and rising limb of all the storm hydrographs except August 2005. In the Duchray catchment, clockwise hysteresis was identified in all of the hysteresis plots, and it is suggested that the soil type and topographic differences are again controlling the concentrations of DOC. We can see the influence of soil type and topography when we consider how the flow paths changes during storm events following wet antecedent conditions. At the start of the event the catchment soil is already wet, and the groundwater level has increased. Soil which the water is moving through therefore contains higher DOC concentrations and DOC concentrations increase more rapidly on the rising limb than during storm events following dry antecedent conditions. The dominance of the clockwise hysteresis in the Duchray catchment, is perhaps due to the greater proportion of mineral soils in the Duchray catchment, resulting in a more rapid depletion of the available DOC and the steeper slopes in the Duchray could potentially decrease the time taken for the flow paths to change to overland flow, resulting in a reduction in DOC concentration. In the Elrig catchment, where organic soils dominate, there is a greater supply of DOC and therefore DOC stores take longer to be depleted and clockwise hysteresis does not always occur.

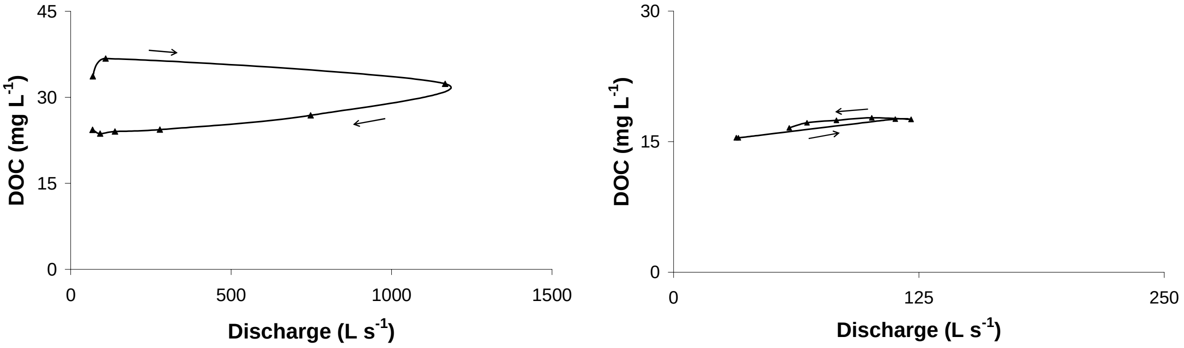
a) March 2005

b) May 2005



c) August 2005

d) December 2005



e) December 2005

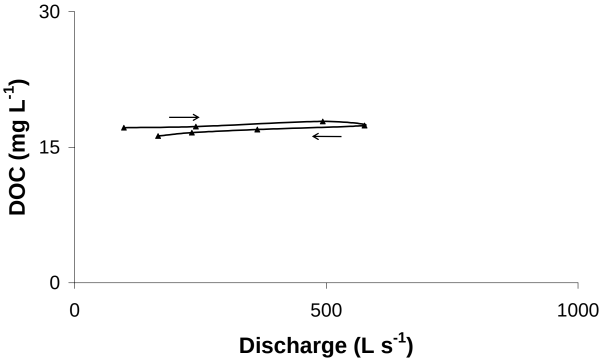


Figure 52: Hysteresis loops of dissolved organic carbon (DOC) plotted against discharge, during storm events following wet antecedent conditions in the Elrig catchment.

To examine how DOC concentrations change during storm events following wet antecedent conditions and how the DOC concentration changes differ from those measured during storms following dry antecedent conditions, three sampling sets sampled in both catchments during May, August and late December 2005 were examined.

Figure 53 shows the results from the May 2005 event in both streams, during which two storm hydrographs were sampled. When the results are compared, it can be identified that DOC concentrations measured in the Elrig were ~10 mg L^{-1} higher than in the Duchray, but a similar range of DOC concentrations were measured throughout the storm event in the Elrig (18.18-29.23 mg L^{-1}) and the Duchray (9.25 – 19.66 mg L^{-1}); and the discharges measured were higher in the Elrig (46-2780 L s^{-1}) than the Duchray (33-1484 L s^{-1}). The first storm hydrograph occurred after 12.4 mm of rain had fallen on the catchments in the previous 5 days. This hydrograph was only partially sampled in both catchments, but anti-clockwise hysteresis was identified in both catchments, the initial DOC concentration on the rising limb of the hydrograph in the Duchray catchment was 9.62 mg L^{-1} and in the Elrig was 21.5 mg L^{-1}, at discharges of 1016 and 2695 L s^{-1}. On the falling limb a larger increase in DOC concentration was measured in the Duchray (17.88 mg L^{-1}), than in the in the Elrig catchment (23.85 mg L^{-1}), at discharges of 1253 and 2243 L s^{-1}. The importance of the antecedent conditions is highlighted when the second storm hydrograph is examined, which took place after 48 mm of rain had fallen on the catchments during the previous five days. During this second hydrograph the DOC concentration exhibited clockwise hysteresis in both catchments. However, a much larger decrease in DOC concentration was measured in the Elrig catchment where concentrations decreased from 29.23 mg L^{-1} two hours before the discharge peak, to 19.84 mg L^{-1} two hours after the peak, at discharges of 494 L s^{-1} and 426 L s^{-1} respectively. In the Duchray catchment a smaller reduction in DOC concentration was measured, reducing from 19.66 mg L^{-1} two hours prior to the peak to 16.65 mg L^{-1} two hours after the peak, at discharges of 197 L s^{-1} and 255 L s^{-1}.

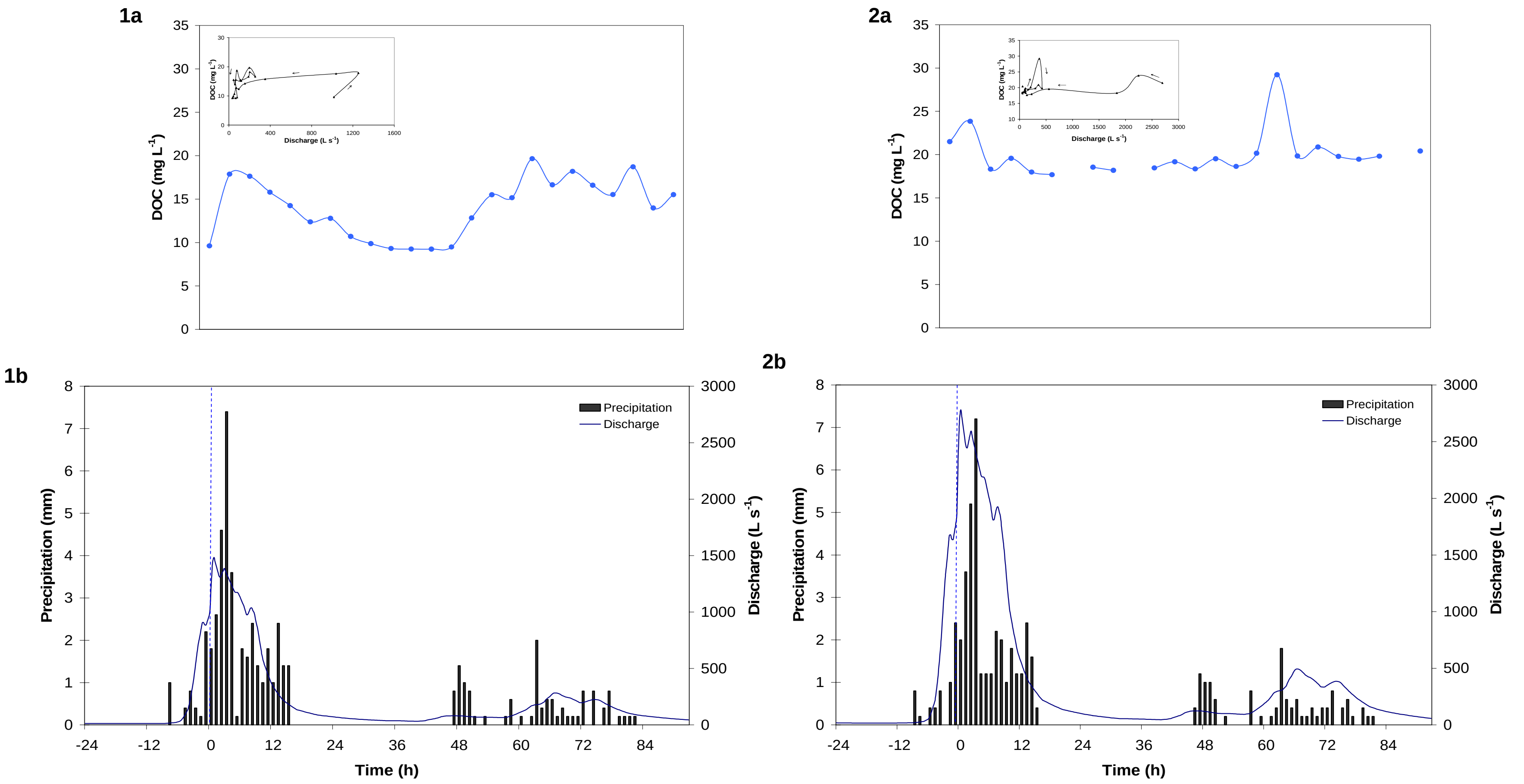


Figure 53: Measurements at the Duchray (1) and Elrig Catchment (2) of a) Dissolved organic carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals between 11.15 am on the 25h May and 07.15 am on the 29th May 2005 in the Duchray and between 11.45 am on the 25th May and 07.45 am on the 29th May 2005 in the Elrig, (three of the samples are missing), inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}), and b) Discharge (L s^{-1}) and precipitation (mm) measurements taken at 15 minute and 1 hour intervals respectively between 11.15 am on the 24h May and 07.15 am on the 29th May 2005 in the Duchray and between 11.45 am on the 24th May and 07.45 am on the 29th May 2005 in the Elrig. The dashed line illustrates when DOC sampling began.

Figure 54 shows the results from the late December 2005 event in both catchments during which two storm hydrographs were sampled. When the results are compared between catchments, it can be identified that a smaller range of DOC concentrations were measured throughout the storm event in the Elrig (15.35-17.86 mg L^{-1}) than the Duchray (10.24-17.16 mg L^{-1}), although a larger peak DOC concentration was measured in the Elrig. However, a greater range of discharges were measured in the Elrig (31-630 L s^{-1}) than the Duchray (17-380 L s^{-1}). Prior to the first storm hydrograph 10 mm of rain had fallen in the catchments during the previous 5 days. During this first hydrograph, anti-clockwise hysteresis was observed in the Duchray, but similar DOC concentrations were measured on the rising and falling limbs of the hydrograph in the Elrig. The DOC concentration on the rising limb was initially lower in the Duchray (15.29 mg L^{-1}) than the Elrig (17.6 mg L^{-1}), at discharges of 98 and 113 L s^{-1}, but a greater increase in concentration was measured on the falling limb in the Duchray (17.16 mg L^{-1}), than in the Elrig catchment (17.56 mg L^{-1}), at discharges of 74 and 121 L s^{-1}. The second larger hydrograph followed was sampled after 14.4 mm of rain had fallen on the catchment in the previous 5 days. During this hydrograph, the DOC displayed clockwise hysteresis in both catchments, although more pronounced in the Duchray catchment. The DOC concentration measured on the rising limb was again lower (16.32 mg L^{-1}) in the Duchray catchment than the Elrig catchment (17.86 mg L^{-1}) at discharges of 324 and 493 L s^{-1}, but in contrast on the falling limb, concentrations decreased in both catchments but the decrease was greater in the Duchray (15.26 mg L^{-1}) than the Elrig (17.41 mg L^{-1}) at discharges of 313 and 576 L s^{-1}. It can also be identified that in both catchments, the DOC concentrations measured during the first and second storm hydrograph were similar, although the second storm hydrograph was of higher magnitude.

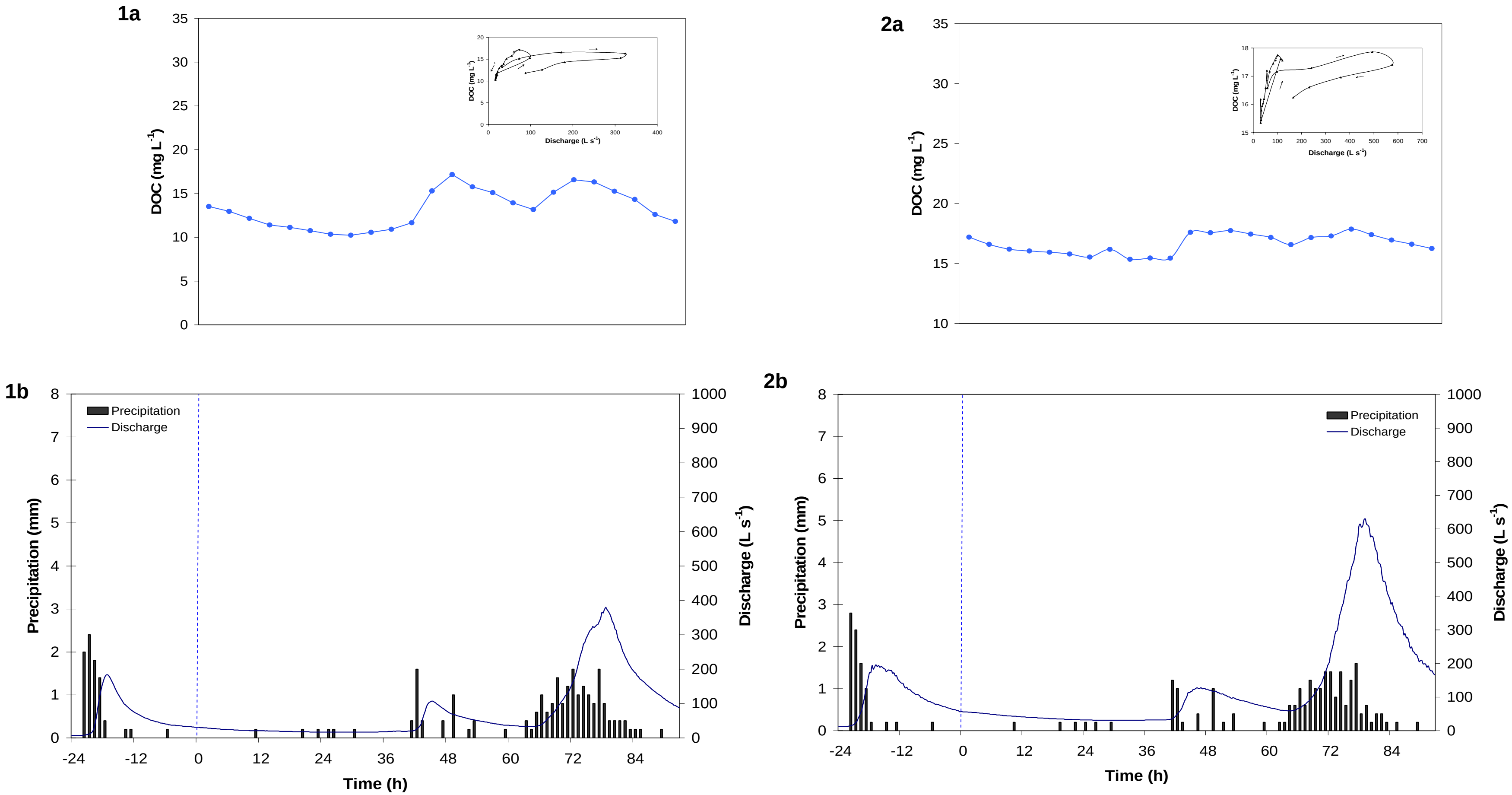


Figure 54: Measurements at the Duchray (1) and Elrig Catchment (2) of a) Dissolved organic carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals between 11.15 am on the 19th December and 7.15 am on the 23rd December 2005 in the Duchray and between 11.45 am on the 19th December and 07.45 am on the 23rd December 2005 in the Elrig, inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}), and b) Discharge (L s^{-1}) and precipitation (mm) measurements taken at 15 minute and 1 hour intervals respectively between 11.15 am on the 18th December and 7.15 am on the 23rd December 2005 in the Duchray and between 11.45 am on the 18th December and 07.45 am on the 23rd December 2005 in the Elrig. The dashed line illustrates when DOC sampling began.

Figure 55 shows the results from the August 2005 event in both catchments, the storm hydrograph sampled, followed wet antecedent conditions within the catchments as 28 mm of rain had fallen in the catchment in the previous 5 days. When the results are compared between catchments, it can be identified that a smaller range of DOC concentrations was measured throughout the sampling event in the Elrig (23.66-36.75 mg L^{-1}) than the Duchray (12.34-32.04 mg L^{-1}), although a larger peak DOC concentration was measured in the Elrig. However, a greater range of discharges were measured in the Elrig catchment (21-1279 L s^{-1}), than the Duchray (9-1000 L s^{-1}). During the storm hydrograph, clockwise hysteresis was observed in both catchments. The degree of hysteresis was greater in the Elrig, as the DOC concentration on the rising limb of the hydrograph was initially lower in the Duchray (31.94 mg L^{-1}) than the Elrig (36.75 mg L^{-1}), at discharges of 109 and 93 L s^{-1}, but the subsequent reduction in concentration on the falling limb was less in the Duchray catchment (28.7 mg L^{-1}) than in the Elrig (26.86 mg L^{-1}), at discharges of 977 and 748 L s^{-1}.

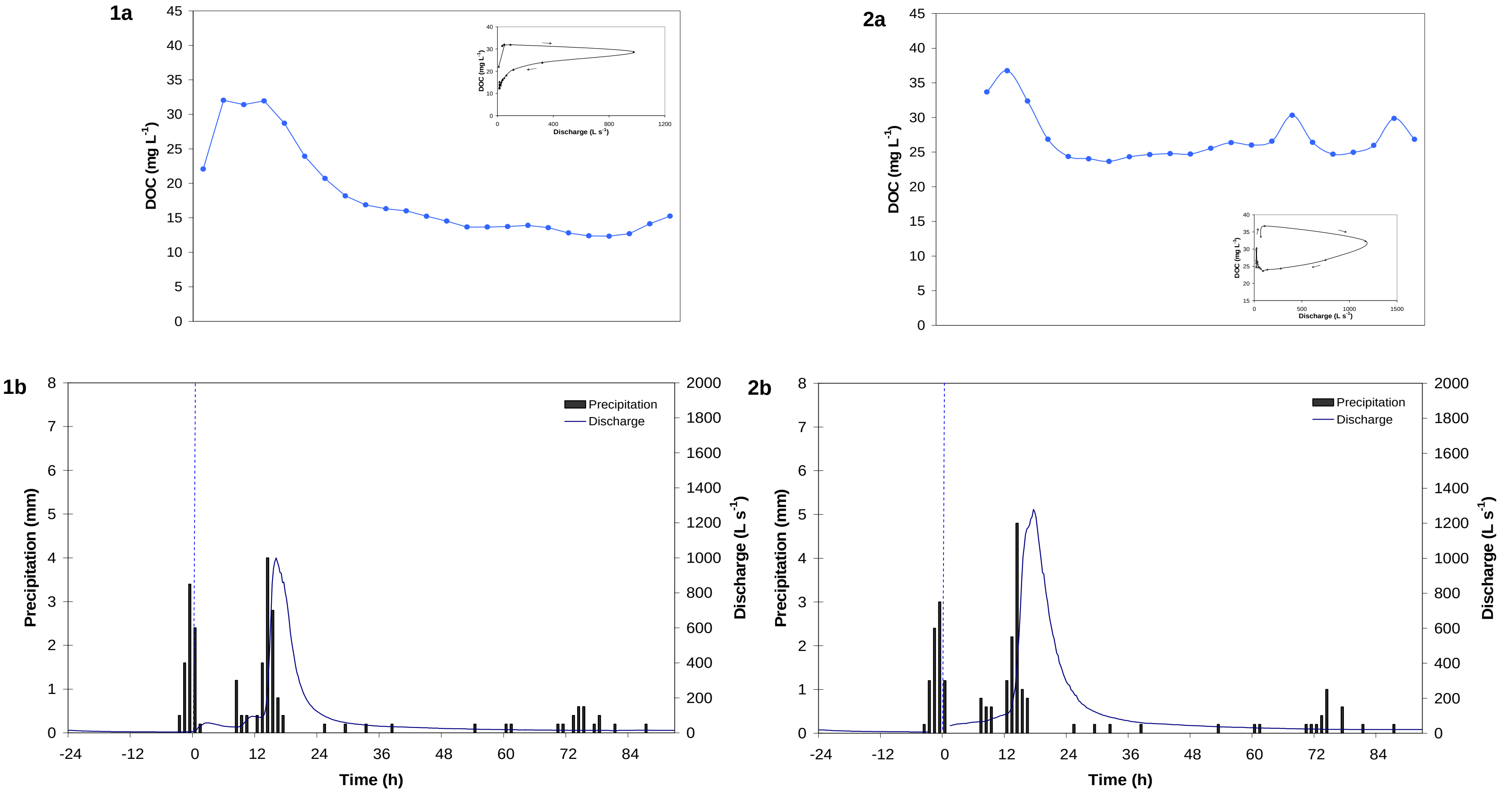


Figure 55: Measurements at the Duchray (1) and Elrig Catchment (2) of a) Dissolved organic carbon (DOC) concentrations (mg L^{-1}), taken at 4 hour intervals between 11.15 am on the 23rd August and 07.15 am on the 27th August 2005 in the Duchray and between 11.45 pm on the 23rd August and 07.45 am on the 27th August 2005 in the Elrig, inserted graph shows DOC (mg L^{-1}) plotted against discharge (L s^{-1}), and b) Discharge (L s^{-1}) and precipitation (mm) measurements taken at 15 minute and 1 hour intervals respectively between 11.15 am on the 22nd August and 07.15 am on the 27th August 2005 in the Duchray and between 11.45 pm on the 22n August and 07.45 am on the 27th August 2005 (discharge data missing between 09.00 am and 12.45 pm on the 23rd August 2005) in the Elrig. The dashed line illustrates when DOC sampling began.

6.3.4.1 Overall difference in DOC concentration between catchments

It was identified that DOC concentrations are greater in the Elrig during all discharges, although the concentrations of DOC measured is closely related to the discharge at the time of sampling. In order to compare the concentrations measured within the two streams directly, mean discharge weighted concentrations were calculated for both catchments. A higher mean DOC concentration was measured in the Elrig catchment (19.97 mg L^{-1}) than in the Duchray (16.70 mg L^{-1}).

6.3.5 Seasonality of the DOC/discharge relationship

To examine the seasonal variation in the data collected from the Elrig catchment, all dissolved organic carbon (DOC) concentrations, corresponding discharges and continuous discharge data were divided into seasons according to previous research (Wilby, 2001; Tank *et al.*, 2005; Pauling and Paeth, 2007), spring (March-May), summer (June-August), autumn (September-November) and winter (December-February). A summary of the data is shown in Table 12. Overall a large range of DOC concentrations was measured in the Elrig, but the range (6.29-39.73 mg L^{-1}) was smaller than that measured in the Duchray (3.93-46.35 mg L^{-1}). DOC concentrations also varied between the seasons. The mean and median DOC concentrations were lowest in the winter, increased through the spring and summer, and were highest during the autumn. In comparison with the Duchray results, much higher mean and median DOC concentrations were measured during all seasons in the Elrig, although the overall range of DOC concentrations was smaller in the Elrig (6.29– 39.73 mg L^{-1}) than the Duchray (3.93 – 46.35 mg L^{-1}).

The range of instantaneous discharges which correspond to the samples taken for DOC analysis covered a wide range of discharges (4-2695 L s^{-1}), but did not cover the full range of discharges that were measured throughout the sampling period (2-3813 L s $^{-1}$). Discharges were higher in the Elrig than the Duchray catchment because the Elrig catchment covers a larger area (1.51 km^2) than the Duchray (0.84 km^2), but in both catchments the samples taken did not cover the full extent of the discharges measured. When examining the instantaneous discharges during the seasons in the Elrig catchment, it can be identified that the magnitude of the discharges change during the seasons, with the smallest mean discharge measured during the autumn, which then increased in the winter and summer and was greatest in the spring. However, the lowest median discharge which would be expected was in the summer; this increased in the autumn and winter and the greatest median discharge was measured during the spring. It should again be noted that only a small number of samples were taken during the autumn.

When the instantaneous discharges were compared with the overall seasonal discharges, a different seasonal discharge pattern was seen. The lowest mean and median discharges were measured during the summer; however a good range of summer discharges were sampled in this study. The mean and median discharges increased during the spring, but for the samples taken during this study, the mean and median discharges were greater, as the samples were taken at a range of discharges, which virtually covered the range of discharges measured during the spring. The autumn period had the next greatest mean and median discharges, however limited samples were taken during this period, therefore both the mean and median and range of instantaneous discharges sampled were low. The greatest mean and median discharges were measured during the winter, however a limited number of high discharge events were sampled in this study, and therefore the instantaneous mean and median were much lower. The difference between the overall discharges measured in the Elrig catchment, and the range of discharges sampled in this study suggest that the samples taken may not be fully representative of the potential DOC concentrations measured in the Elrig catchment, specifically during the autumn and winter.

Table 12: The mean, median and ranges of dissolved organic carbon (DOC) and the corresponding instantaneous discharges and all discharges (taken at 15 minute intervals) measured at the Loch Ard Elrig catchment during spring, summer, autumn and winter and the overall mean, median and range.

Season	Descriptive Statistics	DOC (mg L^{-1})	Instantaneous Discharges	All discharges (L s^{-1})
Spring	Mean	17.24	230	71.69
	Median	19.11	51	25
	Range	8.42 – 29.23	4-2695	4 – 2780
		(n=67)	(n=67)	(n=8820)
Summer	Mean	27.48	64.7	42.26
	Median	26.86	18	9
	Range	21.52 – 39.73	6-1167	2 – 3813
		(n=87)	(n=87)	(n=17645)
Autumn	Mean	32.9	27.5	86.443
	Median	32.97	29	36
	Range	32.29 - 33.5	22-30	7 – 1793
		(n=6)	(n=6)	(n=15746)
Winter	Mean	12.95	61.59	101.23
	Median	13.7	31	45
	Range	6.29 – 17.86	15-576	7 -2742
		(n=88)	(n=88)	(n= 14448)
Total	Mean	19.69	107.4	74.160
	Median	19.48	25	24
	Range	6.29 – 39.73	4 – 2695	2-3813
		(n=248)	(n = 248)	(n=56659)

To examine the seasonal patterns in the relationship between DOC concentrations and the log of discharge (log Q) in the Elrig, the scatterplots shown in Figure 56 were plotted for each of the seasons and the Pearson's product moment correlation coefficient was calculated for each season (all discharges were logged prior to the calculation). The results of the correlations are shown in Table 13 where the results from the correlation between DOC and log Q in the Duchray are also shown.

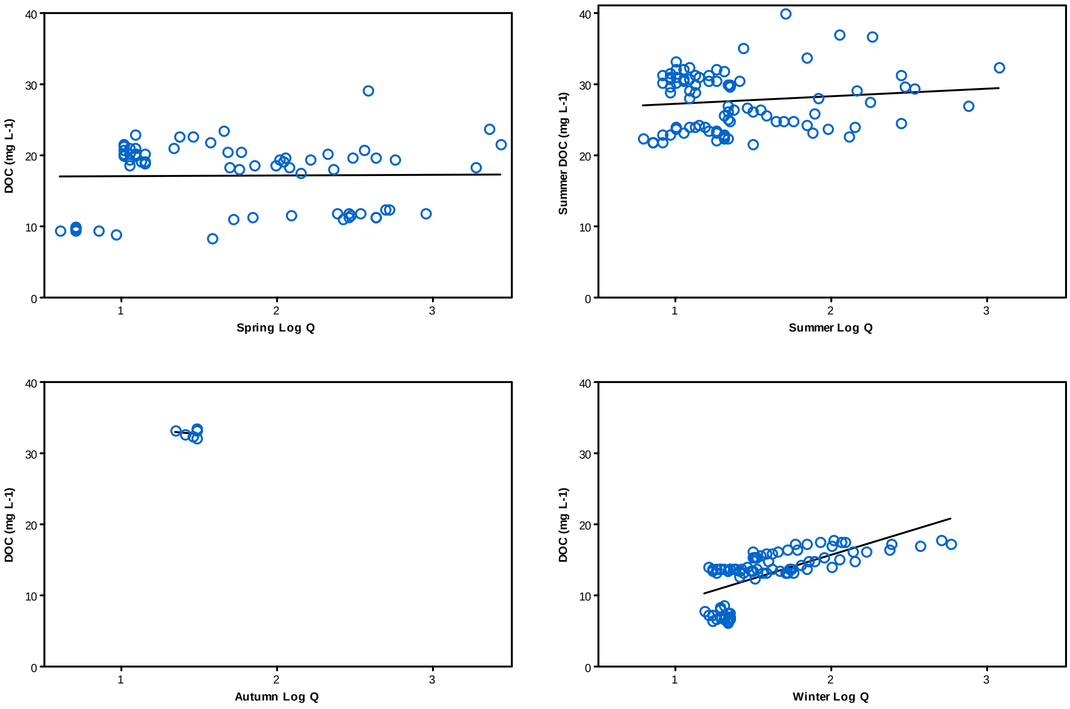


Figure 56: Scatterplots of dissolved organic carbon (DOC) plotted against the log of discharge (Q) produced from results taken from the Elrig catchment, separated by season (spring (R^2=0.00), summer (R^2=0.02), autumn (R^2=0.00) and winter (R^2=0.45)).

The scatterplots shown in Figure 56 suggest weak relationships between DOC and log Q, during all the seasons except winter, although too few samples were taken during the autumn to see any relationship. This is confirmed in Table 13 where it can be observed that all the seasonal Duchray correlations are significant; however in the Elrig catchment, the only significant correlation was during the winter, but the correlation was still weaker than that during the winter in the Duchray. It could be suggested that the limited number of samples collected in the Elrig weakened the DOC/log Q relationship during the seasons, which is perhaps the case during the autumn where too few samples were taken to develop a relationship.

However, during the spring and summer months, an extensive range of DOC concentrations were measured over a wide range of discharges and the DOC/log Q correlations were still weak, suggesting that factors other that season are important in controlling DOC concentrations in the Elrig catchment, but in the Duchray catchment season is still important.

Table 13: Comparison of seasonal differences in the Pearson's product moment correlation coefficient calculated to examine the relationship between dissolved organic carbon (DOC) and the log of discharge in the Duchray and Elrig catchments.

Season	**Duchray**	**Elrig**
Spring	r =0.594, df =70, P<0.01 **R^2=0.35**	r =0.013, df=65 , p=0.918 **R^2=0.00**
Summer	=0.465, df =86, P<0.01 **R^2=0.22**	r=0.126, df = 85, p=0.243 **R^2=0.02**
Autumn	r =0.436, df =99, P<0.01 **R^2=0.19**	r = -0.227, df= 4, p=0.666 **R^2=0.00**
Winter	r =0.756, df =92, P<0.01 **R^2=0.57**	r =0.669, df=86, p=<0.01 **R^2=0.45**
Overall	r = 0.218, df = 353, P<0.01 **R^2=0.05**	r =-0.066, df=246, p=0.301 **R^2=0.00**

6.4 Summary of the influence of hydrological processes and season on DOC concentrations measured in the Duchray and Elrig catchments

The concentrations of dissolved organic carbon (DOC) measured within the Duchray and Elrig streams, are controlled not only by the amount of precipitation falling on the catchment and the season, but also by differences in catchment characteristics including soil type and slope, which also play a part in controlling available DOC concentrations and the flowpaths followed during a storm event.

Analysis of the DOC concentrations measured in the two streams showed that a larger range of DOC concentrations were measured in the Duchray than the Elrig. However, the range of discharges was greater in the Elrig, and the overall mean discharge weighted DOC concentration was greater in the Elrig (19.97 mg L^{-1}) than in the Duchray (16.70 mg L^{-1}). This suggests that there is a larger store of DOC within the Elrig catchment and indeed the Elrig catchment does have a higher percentage of organic soils than the Duchray catchment.

The overall DOC/discharge relationship was found to be not significant in the Elrig and significant but weak in the Duchray (R^2=0.045). The poor relationship can be initially explained by the changing relationships identified during different hydrological conditions and during different seasons within the catchments. During baseflow the source of the DOC is groundwater, the concentration of DOC measured therefore varied according to the DOC concentration within the groundwater which were consistently greater in the Elrig catchment than the Duchray catchment; suggesting that there is a larger store of DOC within the Elrig catchment, reflecting generally deeper peat soils.

During storm events that followed dry antecedent conditions, the dominant direction of DOC hysteresis was anti-clockwise in both catchments, signifying that similar hydrological flowpaths are being followed in both catchments. During the events, as the groundwater level increases the flow path changes to sub-surface throughflow, resulting in higher DOC concentrations measured on the falling limb of the hydrograph. The initial increase in DOC concentrations was quicker in the Duchray than the Elrig, indicating a more readily available supply of DOC in the Duchray catchment. However, concentrations also decreased more rapidly in the Duchray during the storm events, suggesting that a larger store of DOC is available in the Elrig catchment, or alternatively the steeper slopes in the Duchray may cause a more rapid change to overland flow and reduction in DOC concentration.

During storm events that followed wet antecedent conditions the dominant direction of hysteresis was clockwise. When the soil is wet, DOC initially moves to the stream via subsurface throughflow. As the storm progresses and the soil becomes saturated, potential for overland flow will increase and DOC concentrations decrease. The larger reduction in DOC concentration during the May and August 2005 events, compared to events following dry antecedent conditions in the Elrig, suggests that the DOC available within the Elrig catchment is not unlimited and some exhaustion of DOC may be occurring during these events. However, it is also possible again that it is the intensity of the storm event has changed the hydrological flowpaths and overland flow is occurring.

The amount of precipitation falling on the catchments was identified to be important in controlling the movement of DOC from the catchments soil to the stream. However, season should also be acknowledged as a driver of DOC variations within both catchments. Distinct seasonal patterns were identified in both catchments, with the greatest mean, median and range of concentrations measured during the summer, with smaller but similar concentrations measured during the autumn. This pattern was however less established in the Elrig due to the limited number of samples taken during the autumn.

Chapter 7 - Empirical modelling of dissolved organic carbon (DOC) concentrations

7.1 Introduction

The modelling of dissolved organic carbon (DOC) concentrations within water bodies has been successfully used to identify and quantify the factors controlling variations in DOC concentrations in a range of catchments (Grieve, 1991b; Boyer *et al.*, 1996; Dillon and Molot, 1997; Hejzlar *et al.*, 2003). To model variations in DOC concentration, the variables that control the production and movement of DOC must be identified. The variables used within previous models have included the hydrology of the catchment (Boyer *et al.*, 1996) in conjunction with climate parameters (Grieve, 1991a; Hejzlar *et al.*, 2003), other parameters, such as the percentage peat cover within the catchment have also been used (Dillon and Molot, 1997). Once the variables have been identified, they can then be used to model DOC concentrations. Previous modelling techniques have ranged from simple linear (Dillon and Molot, 1997) and multiple linear regression models (Hejzlar *et al.*, 2003) to more complex modelling techniques (Grieve, 1991b; Boyer *et al.*, 1996;). Previous research at the sites monitored in this study; the Ochil Hills catchment during the early 1980s (Grieve, 1984a) and the Loch Ard catchments during the early 1990s (Grieve, 1994), identified a range of variables potentially important in the production and movement of DOC within the catchments, and temperature, precipitation and soil hydrology were identified as important variables in the Ochil Hills and the Duchray and Elrig catchments in chapters 4-6. These variables will be used to produce predictive empirical models of DOC, which will be compared with the models produced during the previous studies to test hypothesis 3 that DOC production has increased due to increases in temperature and/or reductions in acidic deposition since previous research was conducted at the same sites in the early 1980s and 1990s. The results will also be used to test hypothesis 4, that the slope of the DOC/discharge regression will show a greater change in the forest catchments than in the moorland catchment.

This chapter is split into three sections. The first describes the development of the regression models predicting DOC concentration at the Ochil Hills catchment during the early 1980s; these models will be repeated using data collected in the present study. The development of new models predicting DOC concentration will then be discussed, and finally the regression models developed in the 1980s and the present study will be compared. The second section will describe the development of regression models predicting DOC concentration at the Loch Ard catchments during the early 1990s. These models are replicated using data collected in the present study. Finally the regression models developed in the 1990s and the present study will be compared. The final section summarises the results of the modelling section, with the specific aim of identifying if the relationship between DOC concentrations and discharge has changed between the two sampling periods and thereby identifying if DOC concentrations have increased, objective 3 of this study.

7.2 Modelling of dissolved organic carbon (DOC) in the Ochil Hills catchment

Figure 57 compares dissolved organic carbon (DOC) concentrations and discharges measured during the present and previous study. Comparing how DOC concentrations have changed with relationship to discharge is however difficult as samples were taken during different seasons and under different discharges. However, DOC concentrations appear to be higher during the previous study, but peak concentrations were higher in the present study. As direct comparison of DOC concentrations is difficult, the aim of the Ochil Hills modelling section is to identify the variables controlling both the production and movement of dissolved organic carbon (DOC) in order to model DOC concentrations, so direct comparisons can be made over time.

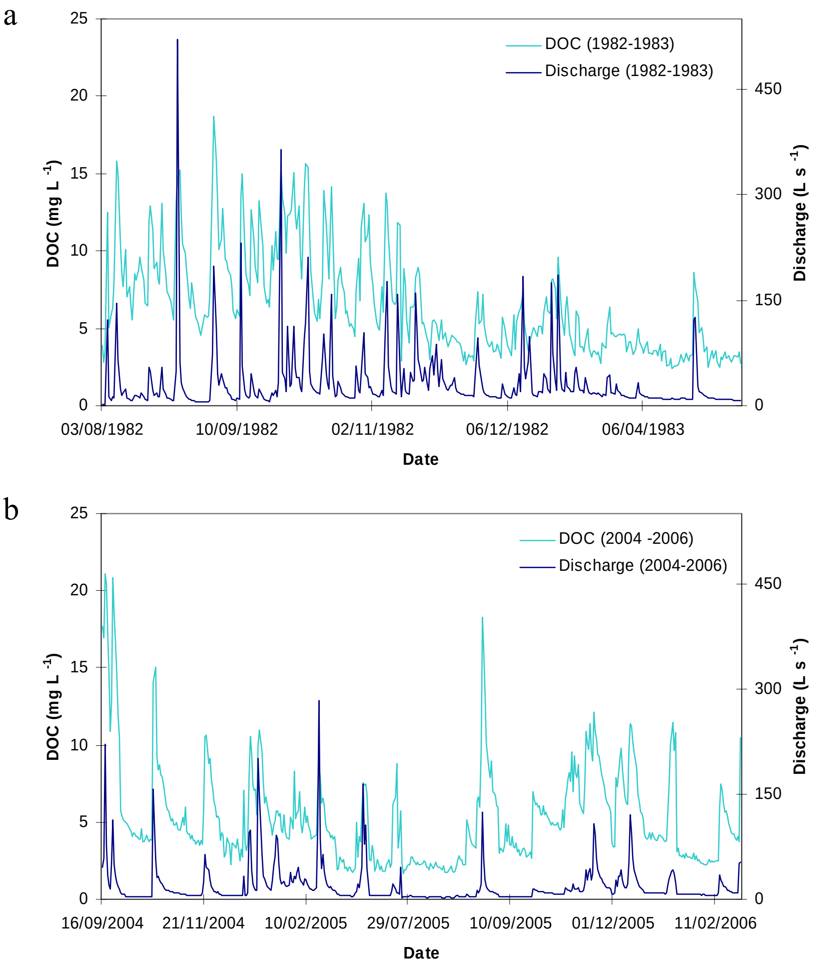


Figure 57: Graphs show dissolved organic carbon concentrations and corresponding discharges measured in the Ochil Hills stream, between a) August 1982 and May 1983, and b) September 2004 and February 2006.

7.2.1 Modelling of dissolved organic carbon (DOC) in the Ochil Hills catchment (1982 -1983)

The Ochil Hills catchment was previously intensively sampled and monitored between June 1982 and June 1983. Streamflow was continuously measured and a meteorological station measured precipitation and air temperature. Water samples were taken at 8 hour intervals, throughout the majority of sampling period. The samples were analysed for their dissolved organic matter (DOM) concentration using the potassium dichromate oxidation method as outlined in Section 3.3.3.1, where 50% of the DOM is assumed to be carbon (Grieve, 1984a). The mean DOC concentration measured in the Ochil Hills catchment (n=355) was 6.64 mg L^{-1}, the median concentration was 5.69 mg L^{-1} and the concentrations ranged from 2.4 to 18.7 mg L^{-1}. The mean discharge (n=355) was 32.3 L s^{-1}, the median was 17.35 L s^{-1} and discharges ranged from 1.41 to 520.98 L s^{-1}.

To model the variation in DOM concentrations within the Ochil Hills catchment, four regression equations were produced (Table 14). The first equation (1) regressed DOM against the log of discharge which only explained 38.5% of the variance in DOM concentration. Grieve (1984a) identified that the residuals from equation 1 showed a seasonal trend when they were graphed against date. A sine wave was fitted to the residual data and sine values were calculated for each week sampled and these values were used in equation 2, greatly improving the fit of the model which now explained 81.5% of the variance. Further improvement was seen, when a coding for the direction of change of stage of the stream at the time of sampling was used (equation 3), which explained 83.5% of the variance. Equation 4 was produced, to determine if the use of temperature data measured at the site, could further explain the variances in DOM concentrations, if used in place of the sine function in equation 3. However this model only explained 78.6% of the variance and therefore equation 3 explained the highest proportion of the variation in DOM concentration. The research that was conducted at the Ochil Hills catchment in the early 1980s has shown it is possible to explain a high proportion of the variance in DOM concentration at the site. As the equations in Table 14, were used to calculate DOM and not DOC concentrations, when the equations are compared all the values within the equation will be halved, as 50% of DOM was assumed to be carbon (1984a).

Table 14: Regression equations for DOM Where DOM is dissolved organic matter (mg l^{-1}); log Q is log (base 10) of discharge ($l\ s^{-1}$); X_1 is sine of the angle [(W+7)*2π]/52, with W as the number of weeks from June 28; X_2 is dummy variable = 1 if stage rising and 0 if falling; X_3 is dummy variable = 1 if stage falling and 0 if rising; T is 14 day mean temperature up to day of sampling (n=577) (after Grieve (1984a).

Regression equation (coefficients ± standard error)	**R^2**
(1) DOM = 0.33+ 7.4 log Q ±0.49 ±0.4	0.385
(2) DOM = -5.1 + 10.8 log Q + 6.5X_1 ±0.3 ±0.2 ±0.2	0.815
(3) DOM = -5.4 + 10.8 log Q + 6.5X_1 – 1.6X_2 + 0.91X_3 ±0.3 ±0.3 ±0.2 ±0.4 ±0.3	0.835
(4) DOM = -11.0 + 10.8 log Q + 0.93 T -1.3X_2 +1.3X_3 ±0.5 ±0.4 ±0.03 ±0.5 ±0.3	0.786

7.2.2 Modelling of DOC in the Ochil Hills catchment (2004-2006)

To determine if the models produced in the previous study at the Ochil Hills catchment are still able to predict DOC concentrations, then the equations (Table 14) produced in the previous study were used to predict DOC concentrations using data collected in the present study and compared to the actual DOC concentrations measured. When compared, similar trends were seen in DOC concentration in both data sets; however the predicted DOC concentration was consistently lower than the actual DOC concentration. This can be observed in Figure 58, where the results from equation 3, the best predictive model from the previous study are shown.

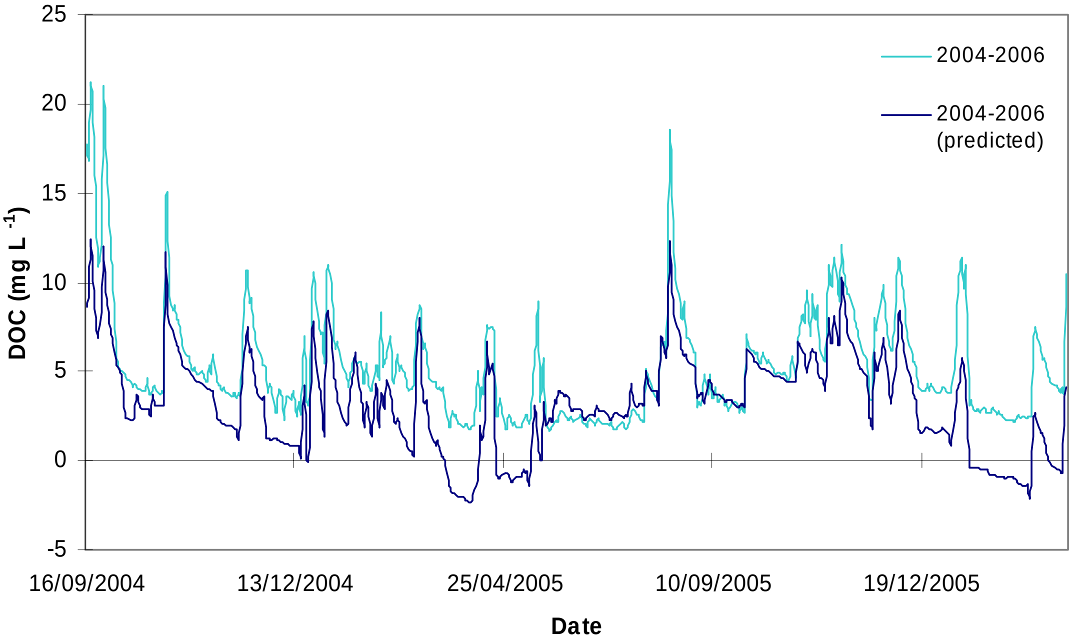


Figure 58: Graph showing dissolved organic carbon (DOC) concentrations, sampled from the Ochil Hills stream between September 2004 and February 2006 and DOC concentrations predicted for the same sampling times using the regression equation, DOC = -2.7 + 5.4log Q + 3.22SI - 0.8X_2 + 0.46X_3 , (Where Q is discharge (L s^{-1}), SI is a seasonal sine index with maximum in September; X_2 is dummy variable = 1 if stage rising and 0 if falling; X_3 is dummy variable = 1 if stage falling and 0 if rising).

The comparison of results identified that the previous models can no longer be used to predict DOC concentrations and new models must be developed. The previous research in the Ochil Hills catchment did however identify several variables that could be used to model DOC concentration. These variables included the log of discharge (log Q), seasonal sine values, falling and rising stage and 14 day average temperatures. To determine if these variables could still be used to model DOC concentration within the Ochil Hills, the regression analysis was repeated using data from the present study. This analysis can also be used to identify which variables are contributing to the changes, if any, in DOC concentration Additional regression models were produced using variables that were not measured during the previous study (water and soil temperature (10 and 30cm)) to identify if any other variable has the potential to model DOC within the Ochil Hills catchment.

7.2.2.1 Discharge

A strong significant relationship between the log of discharge (log Q) and dissolved organic carbon (DOC) concentration was found in the Ochil Hills catchment (DOC (mg L^{-1}) = -0.851 + 5.94 Log Q, $F_{1\ 469}$ = 660.25, P<0.01) as the regression model explained 58.5% of the variation in DOC concentration (chapter 4). Although the model explained a high proportion of the variation in DOC concentration (R^2= 0.59), this relationship could be further improved through the addition of further variables.

7.2.2.2 Seasonal Sine Index

To further improve the regression model, then seasonal sine values were used within the model. Seasonal sine values, were successfully used in the previous study at the Ochil Hills site (Grieve, 1984a) where it was observed that the residuals from the DOC/log Q regression model exhibited a pronounced seasonal trend. When the residuals from the DOC/log Q regression model in this study were plotted (Figure 59), a similar seasonal trend was observed.

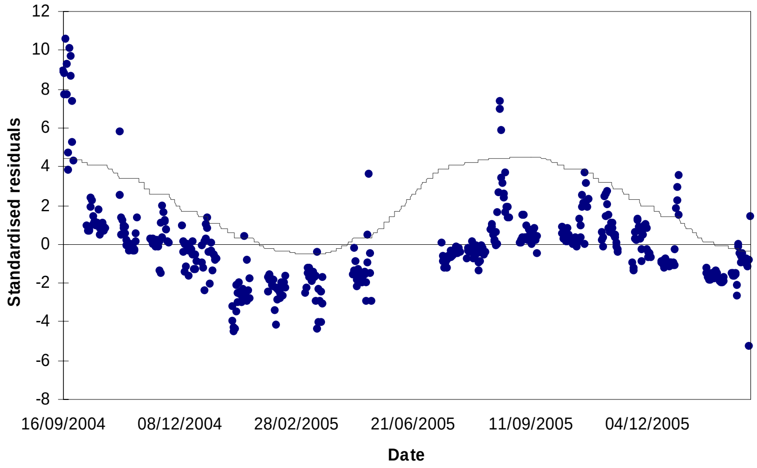


Figure 59: Residuals from the regression of DOC concentration on log Q, also shown by the solid line is the sine wave fitted to the residuals.

A sine wave was then fitted to the residuals which is also shown in Figure 59, sine values for each week used in the study period were then calculated using Equation 7.1 where the highest value (1) was calculated for the week between the 3rd and 9th September and the lowest value (-1) between the 5th and 11th March.

$$Sine = \sin(w * 2\pi)/52 \qquad \textbf{Equation 7-1}$$

w = week number, where week 1 is the 10th to 16th of June

The sine values produced were then used within the regression equation, increasing the variance in DOC explained by the model. The model was significant (DOC (mg L^{-1}) = -2.14 +6.99logQ + 2.11SI, $F_{2\ 467}$ = 848.28, P<0.01), and this model explained 78.4 % of the variance in DOC concentration. The improvement in the model using the sine wave values indicates the importance of seasonality in altering the concentration of DOC measured within the stream. The sine wave is essentially a proxy for temperature (modelled in section 7.2.2.4) and as was previously identified within Chapter 4, pronounced seasonal changes were measured in DOC concentration in the Ochil Hills catchment.

7.2.2.3 Rising and Falling Stage

A small improvement in the regression relationship was identified in the previous research, when a coding for direction of the stage of the stream was used within the regression equation. The coding was used because anti-clockwise hysteresis of DOC concentrations during storm events, was identified during the previous research at the Ochil Hills site (Grieve, 1984a), and was also identified in the present study. The coding of the stage of the stream takes into account when the sample was taken within the storm hydrograph, thereby encompassing the effects of anti-clockwise hysteresis on DOC concentration in the regression equation.

To replicate the coding of the direction of stage for the data in the present study, then it was first necessary to determine when the sample was taken within the storm hydrograph. This was achieved through an examination of the discharge records, and the samples were coded as either 0 when the sample was taken at a stable discharge, 1 when the sample was taken on the falling limb of the storm hydrograph and 2 when the sample was taken on the rising limb. This coding of the sampling events, was then used to produce indicator variables in Minitab, creating dummy variables X_2 and X_3, where X_2 is equal to 1 if the stage is rising and 0 if the stage is falling and X_3 is equal to 1 if stage is falling and 0 if stage is rising. The stage will therefore only be important within the equation if it is rising or falling and not at a steady stage which will be represented by 0 in both dummy variables. The use of the indicator values within the equation produced a small improvement in the regression relationship (DOC (mg L^{-1}) = -2.09 + 6.94log Q + 2.08SI -0.618X_2+ 0.367X_3, $F_{4\ 465}$ = 443.69, P<0.01), now explaining 79% of the variance. The relationship was overall significant; however the X_3 variable was not.

7.2.2.4 Daily Air temperatures

In the previous study (Grieve, 1984a), when 14 day mean temperatures, were used in the regression equation in the place of the seasonal sine values as an index of biological production and decomposition (Grieve, 1984a), the strength of the relationship decreased. To see if the same reduction was measured using the present data, the equation was repeated using the 2004-2006 data. The temperatures used to calculate the 14 day mean temperatures in the Ochil Hill catchment were mainly recorded at the meteorological station installed within the Ochil Hills catchment. The station was however not installed within the catchment until January 2005 after sampling had began. To produce a full temperature record covering the whole sampling period, daily mean temperatures measured at the University of Stirling's meteorological station were used to predict daily mean temperatures for the Ochil Hills catchment. To achieve this, daily mean temperatures recorded during 2005-2006 at the Ochil Hills catchment and corresponding temperatures from the University of Stirling were collated, a linear regression was then produced where the Ochil Hills data was the dependent variable. A strong relationship was identified between the Ochil Hills and the University of Stirling's data (Ochil Hills air temperature = -1.15 + 0.947 * University of Stirling air temperature, $F_{1\ 309} = 11191.46$, $P<0.01$), and the model explained 97.3% of the variance in the Ochil Hills air temperature. The regression equation was then used to calculate daily mean temperatures for the period prior to installation of the meteorological station and to fill in any other missing data. 14 day average temperatures were calculated and were used in place of the sine values in equation 3, as well as the log of discharge (log Q) and the X_2 and X_3 dummy variables representing falling and rising stage. However, little improvement was seen in the model (DOC (mg L^{-1}) = $-5.20 + 7.76\log Q + 0.359T - 0.396X_2 + 0.529X_3$, $F_{4,\ 402} = 400.71$, $P<0.01$), but 80% of the variance in DOC concentration was now explained. The relationship was overall significant; however the X_2 variable was not.

7.2.2.5 Other Variables

The regression equations that repeated the regression analysis used in the previous study at the Ochil Hills catchment produced several strong predictive models. To determine if other variables could improve these models, variables not measured during the previous study were used in a series of best subset regressions. The first best sub-set regression uses discharges averaged over 1, 2, 3, 4, 5 and 6 hours and then a series of best sub-set regressions use air, soil (10 and 30 cm) and water temperatures variables averaged over different time periods as listed in Table 15.

Table 15: Variables and time intervals used to model the concentration of DOC within the Ochil Hills catchment. The sampling intervals within the table refer to the period of time prior to the DOC value used within the model.

	Time interval								
Variable	Instantane -ous	1 hr	2 hr	3 hr	4 hr	5 hr	6 hr	7 Days	14 Days
Dissolved Organic Carbon (mg/L)	✓	×	×	×	×	×	×	×	×
Discharge (L/s and log)	✓	✓	✓	✓	✓	✓	✓	×	×
Air Temperature (°C)	✓	✓	✓	✓	✓	✓	✓	✓	✓
Average Water Temperature (°C)	✓	✓	×	×	×	×	×	✓	✓
Average Soil Temperature (10cm) (°C)	✓	✓	×	×	×	×	×	✓	✓
Average Soil Temperature (30cm) (°C)	✓	✓	×	×	×	×	×	✓	✓

1) Discharge

A strong relationship was identified between dissolved organic carbon (DOC) concentrations and the instantaneous log of discharge (log Q) ($R^2 = 0.59$). However, the instantaneous log Q used in the regression equations is not representative of the discharge that initially produced the DOC. Previous discharges may have been higher, and therefore would have produced higher concentrations of DOC then would be considered normal for the instantaneous discharge. How this relationship can change on the falling and rising limb of the storm hydrograph was previously discussed and indicator variables (X_3 and X_3) were used to represent these changes and increased the strength of the model. To examine this relationship more closely a best-subset regression was performed using 1, 2, 3, 4, 5 and 6 hour average log Q prior to sample extraction. The best subset regression identified that the strongest relationship existed between DOC and the 4 hour log Q (R^2 = 0.62), improving the relationship between DOC and instantaneous log Q (R^2 = 0.59). To examine how the model could be improved further, best sub-set regressions were performed using air, soil (10 and 30cm) and water temperatures.

2) Air, soil (10 and 30 cm) and water temperatures

Seasonal patterns of dissolved organic carbon (DOC) concentrations have been previously identified in the Ochil Hills catchment and the importance of temperature on the production of DOC within the soil is well established (Andersson *et al*., 2000; Andersson and Nilsson, 2001; Neff and Hooper, 2002) indicating the importance of temperature, representing DOC production within the regression equation. Therefore, to expand on the regressions previously produced, temperature variables that were not measured in the previous study including 10 and 30 cm soil temperature and the stream water temperature were used within the regression model. Using these data a series of best sub-set regressions were performed, using the instantaneous data (collected concurrently with sample) and the average 1 hour, 1 day, 7 days and 14 days prior to the sample was taken. The different best sub-set regressions were also used because the number of data points was limited for some variables, specifically the temperature data averaged over 7 and 14 days. The data were limited due to technical problems, which reduced the number of measurements taken by the meteorological station. These temperature variables will be examined to determine if they can improve the model, along with the 4 hour average log Q which was identified to be the strongest discharge related variable in the model, and instantaneous log Q to confirm the importance of using 4 hour log Q within the model.

a) Instantaneous temperatures

The first best sub-set regression shown in Table 16, used all the instantaneous temperature data available (n=320). The regression confirmed the importance of using the 4hr log Q within the regression as the R^2 value for the 4 hour log Q was shown to be greater than the log Q R^2 value. When the 4 hour log Q, was combined with the 10 and 30 cm soil temperatures, the R^2 value was substantially improved. The air and water temperatures were not selected by the best sub-set regression however when the temperatures were used in individual regression equations, where DOC was the dependent variable and 4hr log Q and the air and water temperature were the independent variables, a similar R^2 value was calculated for the water temperature (R^2= 0.823) but the air temperature was lower (R^2=0.773).

Table 16: Results of the best sub-set regression for two or less variables (n=320), using instantaneous log Q, 4 hour average log Q, air temperature, water temperature and 10cm and 30cm soil temperature.

Variables	R^2 adj	C-p	s
4hr log Q	68.7	312.5	1.55
Log Q	66.3	360.0	1.61
4hr log Q and 30cm soil temperature	83.9	7.9	1.11
4hr log Q and 10cm soil temperature	83.7	11.3	1.12

b) 1 hour average temperatures

The second best sub-set regression model shown in Table 17, used a reduced number of data points than the first (n = 296), however similar relationships were identified. Again, the 4 hour log Q had a greater R^2 value than the log Q, and the 10 and 30 cm soil temperatures were identified as strong predictive variables within the model. All R^2 values increased in this regression and it would therefore appear that using 1 hour averages increased the predictive power of the model. However, it is suggested that there will be minimal differences between instantaneous and hourly temperatures, and as the R^2 values for log Q and 4hr log Q also increased, the reason for the increased R^2 values is potentially due to the reduction in sample number. Individual regressions of air and water temperatures again calculated lower R^2 values of 0.855 for water temperature and 0.808 for air temperature.

Table 17: Results of the best sub-set regression for two or less variables (n=296), using instantaneous log Q, 4 hour average log Q, 1 hour average air temperature, 1 hour average water temperature and 1 hour average 10cm and 30cm soil temperature.

Variables	R^2 adj	C-p	s
4hr log Q	74.4	33.8	1.44
Log Q	71.5	402.3	1.52
4hr log Q and 1 hour average 30cm soil temperature	87.4	15.4	1.01
4hr log Q and 1 hour average 10cm soil temperature	87.1	24.6	1.02

c) 1 day average temperatures

The third best sub-set regression shown in Table 18 used 1 day average temperatures, the results were found to be the same as the 1 hour average temperature best-sub set regressions, with 10 and 30cm soil temperatures again identified as strong predictive variables of the regression. When the water and air temperatures were individually used within the regression equation then lower R^2 values were again found for air temperature (R^2 =0.838), but a similar value was found for water temperature (R^2=0.863).

Table 18: Results of the best sub-set regression for two or less variables (n=296), using instantaneous log Q, 4 hour average log Q, 1 day average air temperature, 1 day average water temperature and 1 day average 10cm and 30cm soil temperature.

Variables	R^2 adj	C-p	s
4hr log Q	74.4	313.2	1.44
Log Q	71.5	379.5	1.52
4hr log Q and 1 day average 30cm soil temperature	87.5	3.7	1.00
4hr log Q and 1 day average 10cm soil temperature	87.3	9.1	1.02

d) 7 day average temperatures

The fourth best sub-set regression shown in Table 19 used 7 day average temperatures, the results were found to be the same as the previous models, with 10 and 30cm soil temperatures again identified as strong predictive variables within the regression. When the water temperature and air temperature were individually used within the regression equation, the R^2 values for air temperature is now similar (R^2 =0.857) to the soil temperature R^2 values, as is the water temperatures (R^2=0.862).

Table 19: Results of the best sub-set regression for two or less variables (n=260), using instantaneous log Q, 4 hour average log Q, 7 day average air temperature, 7 day average water temp, 7 day average 10cm soil temperature and 7 day average 30cm soil temperature

Variables	R^2 adj	C-p	s
4hr log Q	75.2	217.8	1.45
Log Q	72.0	277.2	1.53
4hr log Q and 7 day average 30cm soil temperature	86.2	8.2	1.08
4hr log Q and 7 day average 10cm soil temperature	86.8	12.9	1.07

e) 14 day average temperatures

The fifth best sub-set regression shown in Table 20 used 14 day average temperatures which were previously identified to strengthen the regression model. In this best sub-set regression the variables identified to be important were 14 day average air and water temperature. However, when individual regressions were performed using the 10 and 30cm soil temperatures similar R^2 values of 0.864 and 0.865 respectively, were produced.

Table 20: Results of the best sub-set regression for two or less variables (n=248), using instantaneous log Q, 4 hour average log Q, 14 day average air temperature, 14 day average water temp, 14 day average 10cm soil temperature and 14 day average 30cm soil temperature

Variables	R^2 adj	C-p	s
4hr log Q	75.7	208.4	1.44
Log Q	73.5	249.9	1.50
4hr log Q and 14 day average water temperature	86.6	7	1.07
4hr log Q and 14 day average air temperature	86.5	8.5	1.07

3) Summary

The five best sub-set regressions identified that the strongest variables used to model dissolved organic carbon (DOC) were consistently the 4 hour log Q and the 10 and 30cm soil temperatures. However, little difference in the strength of the model was observed between the different average time periods and it is apparent that the number of data points used within the regression is slightly altering the regression relationship. This is highlighted by the change in the R^2 value of both log Q and 4hr log Q between the different time periods, although the difference is small, the lowest R^2 value for both variables was observed during the best sub-set regression of the instantaneous values. The lowest R^2 value for the 10 and 30cm soil temperatures were also measured for the instantaneous values. The difference between the variables used also seems to be minimal, although a lower R^2 value was found when air temperature was used in the instantaneous, 1 hour average and 1 day average air temperatures, suggesting that average air temperatures should only be used over longer time periods and the soil temperature is more representative of DOC production within the soil over shorter time scales. The results of the best sub-set regressions do however highlight the importance of using temperature as a parameter within the regression model and improvements on the previous models can be observed; the strongest relationship identified was the 4hr log Q and 1 day average 30cm soil temperature (R^2 =0.875). This model also explained more of the variance in

DOC concentration than the model produced using the seasonal sine values which explained 78% of the variance.

7.2.3 Comparison between DOC concentrations modelled between 1982-1983 and 2004-2006 in the Ochil Hills catchment

To identify if dissolved organic carbon concentrations (DOC) have changed over time in the Ochil Hills catchment and if the relationship between DOC and the variables used within the models have changed, the regression equations produced in the previous study and the present study will be compared and are shown in Table 21. Equations 1 and 2 from the 1982-83 study are re-produced using a limited data set of 355 samples taken between the 3rd August 1982 and the 2nd May 1983; the regression equations produced were however similar to those developed in the 1982-83 study (see Table 14). Equation 3 and 4 from the 1982-83 study are the original equations from the previous research (corrected to allow calculation of DOC) as the data needed to determine rising and falling stage and temperature are not available. A comparison of the regression equations will be made in the next section.

Table 21: Summary table of all regression equations produced from data collected at the Ochil Hills catchment between 1982-1983 and 2004-2006. Where DOC is in mg L^{-1}, Q is discharge (L s^{-1}), SI is a seasonal sine index with maximum in September; X_2 is dummy variable = 1 if stage rising and 0 if falling; X_3 is dummy variable = 1 if stage falling and 0 if rising; T is 14 day mean temperature up to day of sampling.

Ochil Hills (1982-83) regression equations (coefficients ± Standard error)	**Ochil Hills (2004-2006) regression equations (coefficients ± Standard error)**
(1) $DOC = -1.4 + 4.78 \log Q$ $\pm 0.43 \quad \pm 0.32$ $(R^2=0.392)$	(2) $DOC = -0.851 + 5.94 \log Q$ $\pm 0.26 \quad \pm 0.23$ $(R^2= 0.585)$
(2) $DOC = -1.93 + 5.04 \log Q + 3.02\, SI$ $\pm 0.24 \quad \pm 0.18 \quad \pm 0.11$ $(R^2 = 0.815)$	(2) $DOC = -2.14 + 6.99 \log Q + 2.11\, SI$ $\pm 0.20 \quad \pm 0.17 \quad \pm 0.10$ $(R^2= 0.784)$
(3) $DOC = -2.7 + 5.4 \log Q + 3.22 SI - 0.8X_2 + 0.46X_3$ $\pm 0.15 \quad \pm 0.15 \quad \pm 0.10 \quad \pm 0.20 \quad \pm 0.15$ $(R^2=0.835)$	(3) $DOC = -2.09 + 6.94 \log Q + 2.08\, SI - 0.618X_2 + 0.367X_3$ $\pm 0.21 \quad \pm 0.21 \quad \pm 0.10 \quad \pm 0.22 \quad \pm 0.20$ $(R^2=0.791)$
(4) $DOC = -5.5 + 5.4 \log Q + 0.46T - 0.65X_2 + 0.65\, X_3$ $\pm 0.25 \quad \pm 0.2 \quad \pm 0.02 \quad \pm 0.25 \quad \pm 0.15$ $(R^2=0.786)$	(4) $DOC = -5.20 + 7.76 \log Q + 0.359T - 0.396X_2 + 0.529X_3$ $\pm 0.32 \quad \pm 0.24 \quad \pm 0.02 \quad \pm 0.25 \quad \pm 0.22$ $(R^2=0.797)$

7.2.3.1 Comparison of the relationship between DOC, seasonal sine values, rising and falling stage and 14 day average temperatures

A comparison of the regression equations 1-4 in Table 21 highlights the similarities that exist between the equations produced in 1982-83 and 2004-06, specifically the intercept of the regression line, which shows little variation when the regression equations are compared between years. The greatest difference in the equations is the higher log Q value, and lower temperature, sine and falling and rising stage values. The increase in the value of log Q in the regression relationship suggests that during the present study there is now more DOC available for movement to the stream at the same unit discharge. The reduction in the temperature and sine values suggests that the difference in concentration of DOC being produced during the summer and the winter has decreased which could be explained by increased winter temperatures. To compare the regression equations visually, then the graphs shown in Figure 60 were plotted. The DOC concentrations in the graph were predicted using regression equations 2-4 in Table 21, with the log Q, sine and falling and rising stage values from the present study, all 1982-83 DOC concentrations were converted, as discussed within section 3.4.4 and then DOC was plotted against the log of discharge. Similar patterns can be observed within all the graphs shown in Figure 60; the spread of points around the regression line is greater in all the graphs for the 1982-83 data and the slope of the regression line is slightly steeper in all graphs for the 2004-2006 data, with higher concentrations predicted during the higher discharges. The greatest difference between the regression lines is between the equation 4 graphs. To determine if the change between the time periods was real, then the F-test statistic was calculated for the DOC, log Q and the seasonal sine index relationship (could only be achieved for this regression due to missing data). Using the 1982-83 and 2004-06 data, the calculated F-test statistic (59.79) was found to be greater than the F value of 3.01, suggesting that the relationship between DOC, log Q and the seasonal sine index has changed between the two sampling periods. This suggests, that as no change occurred in the DOC and log Q relationship, then it is the seasonal sine index that has altered the relationship and this is the one variable that had changed in the regression equation, as when the sine wave was fitted to the DOC/log Q regression relationship residuals the peak value was in September, as opposed to August in the previous study (Grieve, 1984a).

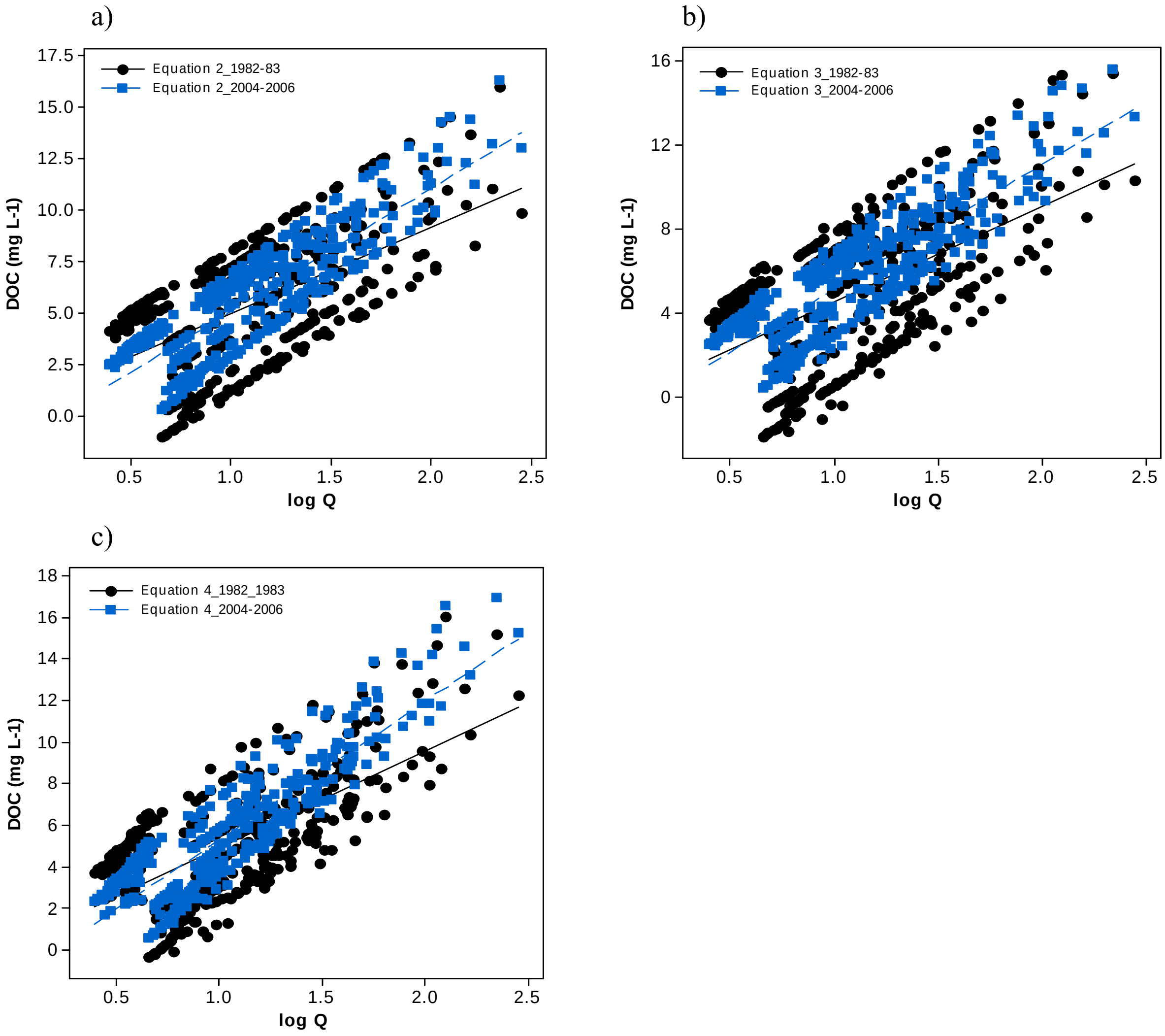


Figure 60: Scatterplots showing the relationship between the log of discharge (log Q) and DOC concentrations from data collected during 1982-1983 and 2004-2006 from the Ochil Hills catchment, DOC concentrations were produced using regression equations with the independent variables a) log Q (L s^{-1}) and a seasonal sine index with maximum in September b) log Q (L s^{-1}), the seasonal sine index and dummy variables $X_2 = 1$ if stage rising and 0 if falling and $X_3 = 1$ if stage falling and 0 if rising and c) log Q (L s^{-1}), the dummy variables (X_2 and X_3) and the 14 day mean temperature up to day of sampling.

7.3 Modelling of dissolved organic carbon (DOC) concentrations within the Duchray and Elrig catchments

Figure 61 compares dissolved organic carbon (DOC) concentrations and discharges measured during the present and previous study in the Duchray and Elrig catchments and clearly show that large increases in DOC concentrations have occurred in both catchments. Comparing how DOC concentrations have changed with relationship to discharge is however difficult, as samples were taken during different seasons, and under different discharges. As direct comparison of DOC concentrations is difficult, the aim of the Duchray and Elrig modelling section is to identify the factors controlling both the production and movement of dissolved organic carbon (DOC) within the Duchray and Elrig catchments, so direct comparisons can be made over time. The previous research at the Duchray and Elrig catchments will be initially discussed; the regression analysis completed during this research will then be repeated using data from this study, and the models will be compared to identify any changes in the relationships

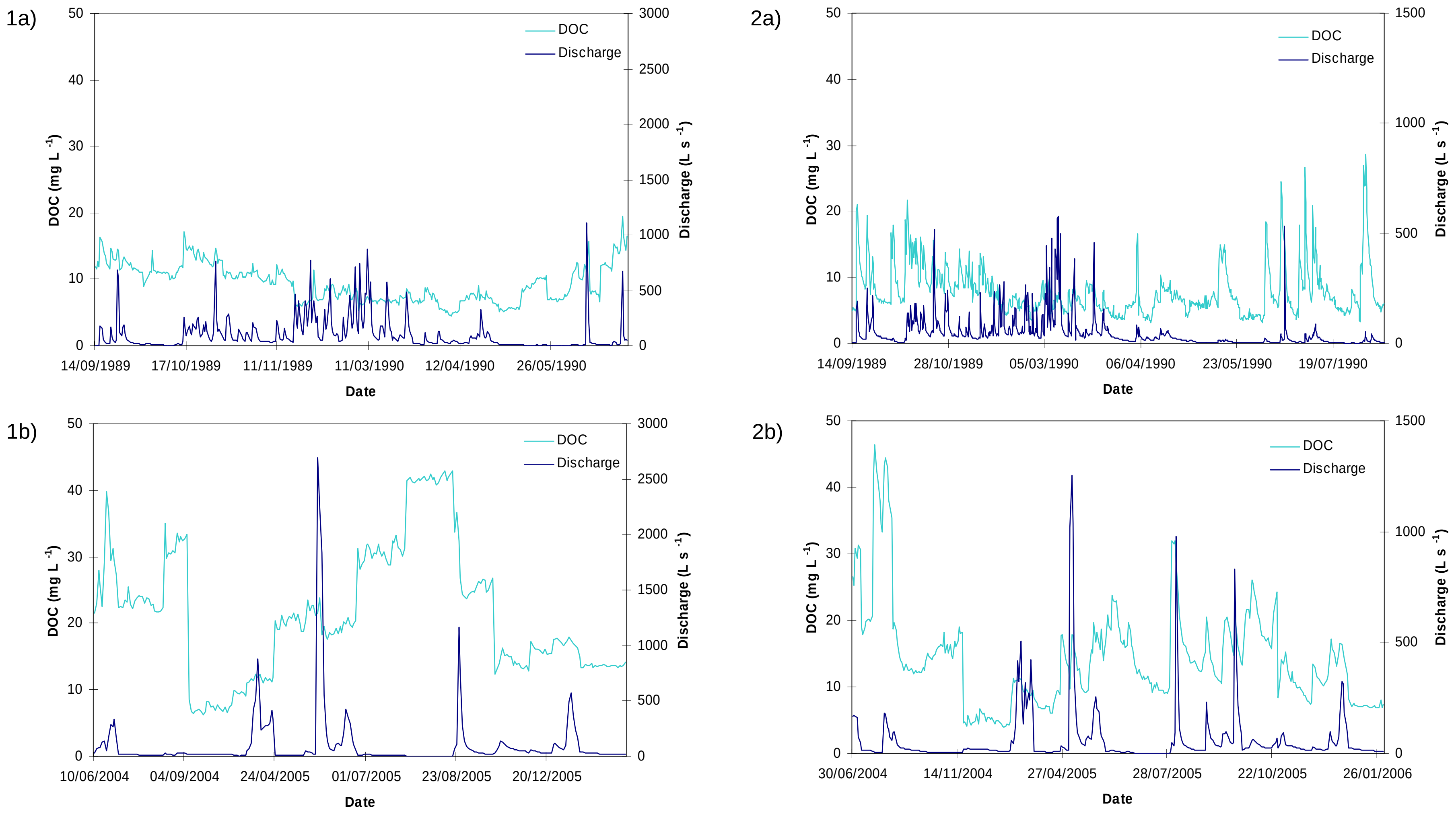


Figure 61: Graphs show dissolved organic carbon (DOC) concentrations and corresponding discharges measured in the 1)Elrig and 2)Duchray stream, between a) September 1988 and June 1990 (Elrig) and August 1990 (Duchray) and b) June 2004 and January 2006.

7.3.1 Modelling of DOC in the Duchray and Elrig catchments (1989 -1990)

The Duchray and Elrig catchments were previously intensively sampled and monitored between September 1989 and August 1990. Continuous discharges were measured throughout the sampling period and water samples were taken from the Duchray at 4 hour intervals and from the Elrig at 8 hour intervals throughout the majority of the sampling period. DOC concentrations in the Duchray (n=820) had a mean concentration of 7.94 mg L^{-1}, a median concentration of 6.8 mg L^{-1} and ranged from 3.2-28.7 mg L^{-1}. The mean discharge (n=820) in the Duchray catchment was 47.42 L s^{-1}, the median was 25 L s^{-1} and discharges ranged from 1 to 577 L s^{-1}. In the Elrig catchment (n=409) the DOC mean concentration was 9.34 mg L^{-1}, a median concentration of 9.1 mg L^{-1} and ranged from 4.4-19.5 mg L^{-1}. The mean discharge (n=409) in the Elrig catchment was 97.35 L s^{-1}, the median was 43 L s^{-1} and discharges ranged from 3 to 1107.0 L s^{-1}

The results from this research have been previously been published by Grieve (1994), and a series of equations which are shown in Table 22 were developed where DOC was regressed on a series of controlling variables. In equation (1) and (2) from Table 22 the dependent variable is all the DOC samples collected during the study period and the independent variables are the corresponding instantaneous discharges and seasonal sine values. When the results of this model are compared, it can be observed that a stronger relationship was found within the Elrig ($R^2 = 0.75$) than in the Duchray ($R^2 = 0.41$). The second equation uses only the results collected when the discharge was greater than 30 L s^{-1} and an additional variable, TD (number of days since the last storm event). The second equation proved to be a better predictor of DOC concentration, with a greater improvement in the model in the Duchray ($R^2 = 0.70$) than the Elrig catchments ($R^2 = 0.83$).

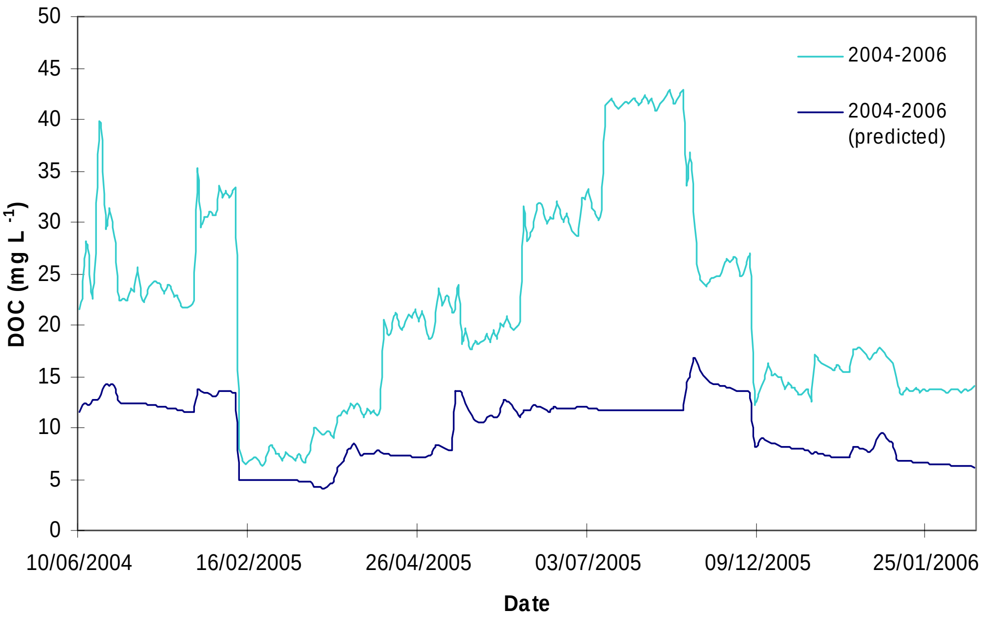
Table 22: Regressions of DOC on controlling variables in the Duchray and Elrig catchments, where DOC is in mg L^{-1}, Q is discharge (L s^{-1}), SI is a seasonal sine index with maximum in August; and TD is number of days since last event (after Grieve (1994))

Equation and Data Used	Equation (coefficients ± Standard error)	R^2
Equation 1:Duchray All data (n=830)	$DOC = 1.20 + 4.86\log(Q) + 4.04SI$ ±0.33 ±0.23 ±0.19	0.41
Equation 1:Elrig All data (n=409)	$DOC = 6.83 + 1.83\log(Q) + 4.3SI$ ±0.20 ±0.12 ±0.12	0.75
Equation 2: Duchray Discharge>30 L s^{-1} (n=263)	$DOC = 3.66 + 3.27\log(Q) + 4.73SI + 0.26TD$ ±0.98 ±0.48 ±0.31 ±0.03	0.70
Equation 2: Elrig Discharge>30 L s^{-1} (n=234)	$DOM = 5.67 + 2.21\log(Q) + 4.21SI + 0.8TD$ ±0.48 ±0.22 ±0.15 ±0.02	0.83

7.3.2 Modelling of DOC in the Loch Ard catchments (2004-2006)

To determine if the models produced in the previous study at the Duchray and Elrig catchments are still able to predict DOC concentrations, then equation 1 (Table 22) was used to predict DOC concentrations using data collected in the present study and compared to the actual DOC concentrations measured and is shown in Figure 62. It can be identified that similar trends were seen in DOC concentration in both data sets; however the predicted DOC concentration were consistently much lower than the actual DOC concentration. Therefore the previous models can no longer be used to predict DOC concentrations and new models must be developed. However, the similarity between fluctuations in DOC are still controlled by the same variables, therefore, the models produced in the previous research will be replicated.

a)



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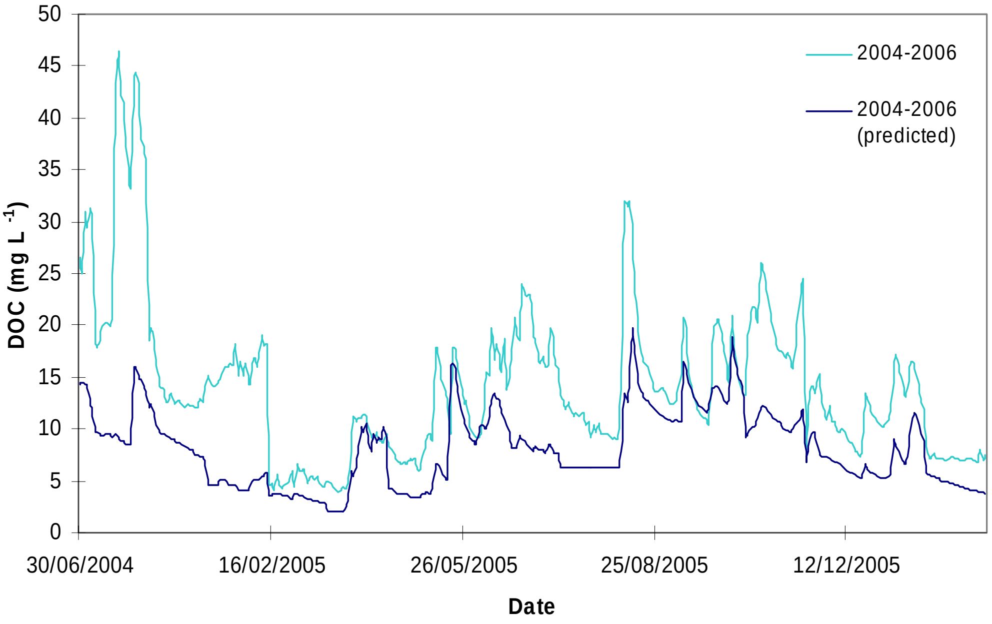


Figure 62: Graphs showing dissolved organic carbon (DOC) concentrations, sampled from the a) Elrig and b) Duchray stream between June 2004 and January 2006 and DOC concentrations predicted for the same sampling times using the regression equations, DOC = 6.83 + 1.83log Q + 4.3SI (Elrig) and DOC = 1.20 + 4.86log Q + 4.04SI (Duchray), (Where Q is discharge (L s^{-1}) and SI is a seasonal sine index with maximum in August).

7.3.2.1 Discharge

The relationship between discharge and dissolved organic carbon concentration (DOC) in both the Duchray and Elrig catchments has previously been discussed within chapters 5 and 6. When a regression was performed using DOC as the dependent variable and the instantaneous log of discharge (log Q), then a weak relationship was identified in the Duchray (DOC (mg L^{-1}) = 10.4 + 2.84 Log Q, $F_{1\ 353} = 17.61$, $P<0.01$) as the model only explained 4.5% of the variance. Within the Elrig catchment the relationship was found to be not significant (DOC (mg L^{-1}) = 21.1 - 0.934 Log Q, $F_{1\ 246} = 1.07$, $P=0.301$) Discharge alone is therefore a poor predictor of DOC concentration and cannot be used to model DOC concentrations within the Loch Ard catchments.

7.3.2.2 Seasonal Sine Index

The use of seasonal sine values within the regression model in the previous study greatly improved the regression equation. To further improve the regression model in this study, a seasonal sine index was produced for both the Loch Ard sites. The production of the seasonal sine index was previously discussed within section 7.2.2.2, and the process was repeated for both the Loch Ard sites where the residuals from equation 1 were plotted and a sine wave was fitted to the residuals as shown in Figure 63. Values for each week used in the study period were then calculated using Equation 7.2. In the Elrig catchment the highest value (1) was between the 12th and 18th August and the lowest value (-1) between the 12th and 18th February. In the Duchray catchment the highest value (1) was between the 18th and 25th August and the lowest value (-1) between the 19th and 25th February.

$$Sine = \sin(w * 2\pi)/52$$ **Equation 7-2**

w = Week number, where week 1 is the 20th to 26th of May in the Elrig Catchment and 27th May to the 2nd June in the Duchray catchment

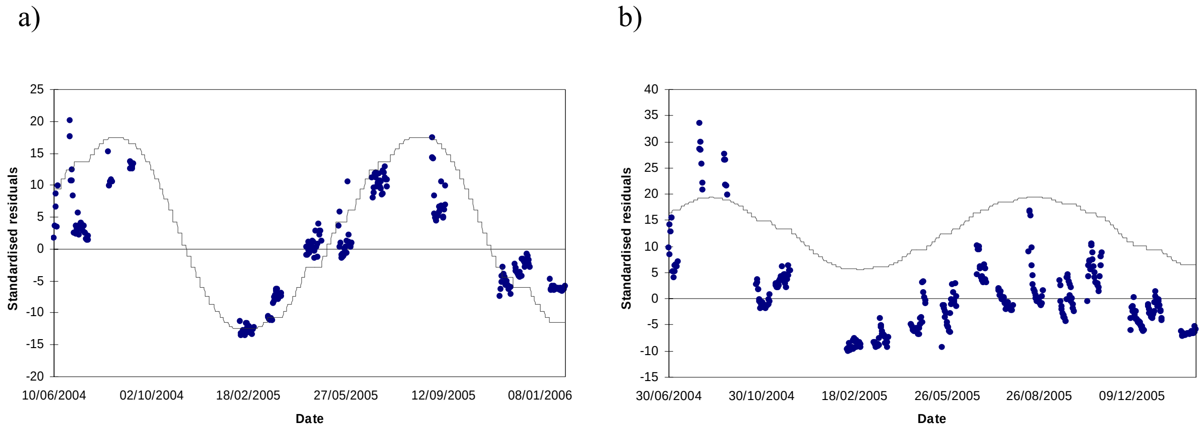


Figure 63: Residuals from the regression of DOC concentration on log Q, also shown by the solid line is the sine wave fitted to the residuals for the a) Elrig and b) Duchray Catchment

The sine values produced were then used within the regression equation, and the addition of the sine variable increased the strength of the model. The model produced was significant in the Duchray catchment (DOC (mg L^{-1}) = 8.26 + 3.92logQ +7.60SI, $F_{2\ 352}$ = 166.42, P<0.01), and now explained 48.3 % of the variance in DOC concentration. A greater improvement in the model was found within the Elrig catchment (DOC (mg L^{-1}) = 19.7 + 0.24 log Q + 9.8SI, $F_{2\ 245}$ = 533.50, P<0.01) where the model now explained 81.2% of the variance in DOC concentration.

7.3.2.3 Number of days since previous storm event (TD)

In the previous study the variable number of days since the previous storm event (TD) was successfully used to model DOC concentrations, greatly improving the R^2 value in both catchments. To repeat this equation using the data collected in this study, the DOC concentrations measured at discharges of greater than 30 L s^{-1} were selected. The number of days since the previous storm event when the discharge was greater than 30 L s^{-1} were then counted, and this figure was then used as the variable TD within the regression equation. When the regression equations were produced, the relationship was not improved in either of the catchments, although the R^2 values were similar to the R^2 value produced for the previous equation using the seasonal sine values. In the Duchray (DOC = 5.63 + 4.55 log Q + 7.88 SI + 0.546 TD, $F_{3\ 114}$ = 33.36, P<0.01), 45.3% of the variance in DOC concentration was explained by the model, and in the Elrig (DOC = 19.3 + 0.443 log Q + 8.97 SI - 0.0223 TD, $F_{3\ 107}$= 113.48, P<0.01) 75.4% of the variance was explained. The overall equations were both significant, however the constant was not significant in the Duchray catchment and log Q and TD were not significant in the Elrig catchment.

7.3.3 Comparison between DOC concentrations modelled between 1989-1990 and 2004-2006 in the Loch Ard catchments

To identify if dissolved organic carbon (DOC) concentrations have changed between the two sampling periods, 1989-1990 and 2004-2006, then the regression analysis completed in the previous study was repeated using the 2004-2006 data. A comparison of the regression equations produced during the two sampling periods are shown within Table 23 and will be discussed within this section. To directly compare the regression equations developed during the two sampling periods, it was necessary to re-produce the regression equations using the 1989-1990 data. The data available for this was however limited to DOC concentrations and instantaneous discharges, therefore only Equations 1 and 2 for both catchments could be re-produced. In order to achieve this sine values were reproduced and then the resulting equation 1 for each of the equations are compared with the previous published equations (Grieve, 1994). The equations were nearly identical to the previous equation in both the Duchray (DOC = 1.20 + 4.88 Log Q + 4.04SI, R^2 = 0.41) and the Elrig (DOC = 6.85 + 1.82 Log Q + 4.31SI, R^2 =0.75).

Table 23: Summary table of all regression equations produced from data collected at the Duchray and Elrig catchments between 1989-90 and 2004-06. Where, DOC is in mg L^{-1}, Q is discharge (L s^{-1}), SI is a seasonal sine index with maximum in August; and TD is number of days since last event.

Equation and Data Used	1989-1990 regression equations (coefficients ± Standard error)	2004-06 regression equations (coefficients ± Standard error)
Equation 1 Duchray	$DOC = 5.01 + 2.17 \log Q$ ±0.34 ±0.23 ($R^2=0.095$)	$DOC = 10.4 + 2.84 \log Q$ ±0.99 ±0.68 ($R^2=0.045$)
Equation: 1 Elrig	$DOC = 8.93 + 0.261 \log Q$ ±0.38 ±0.22 ($R^2=0.003$)	$DOC = 21.1 - 0.934 \text{ Log } Q$ ±1.49 ±0.90 ($R^2=0.00$)
Equation 2: Duchray	$DOC = 1.20 + 4.86 \log (Q) + 4.04SI$ ±0.33 ±0.23 ±0.19 ($R^2=0.41$)	$DOC = 8.26 + 3.92 \log Q + 7.60\,SI$ ±0.74 ±0.50 ±0.44 ($R^2=0.483$)
Equation 2: Elrig	$DOC = 6.83 + 1.83 \log (Q) + 4.3SI$ ±0.20 ±0.12 ±0.12 ($R^2=0.75$)	$DOC = 19.7 + 0.24 \log Q + 9.8SI$ ±0.65 ±0.39 ±0.30 ($R^2=0.796$)
Equation 3: Duchray	$DOC = 3.66 + 3.27 \log (Q) + 4.73SI + 0.26TD$ ±0.98 ±0.48 ±0.31 ±0.03 ($R^2=0.70$)	$DOC = 5.63 + 4.55 \log Q + 7.88\,SI + 0.546\,TD$ ±3.04 ±1.44 ±0.85 ±0.12 ($R^2=0.453$)
Equation 3: Elrig	$DOC = 5.67 + 2.21 \log (Q) + 4.21SI + 0.8TD$ ±0.48 ±0.22 ±0.15 ±0.02 ($R^2=0.83$)	$DOC = 19.3 + 0.443 \log Q + 8.97\,SI - 0.0223TD$ ±1.43 ±0.68 ±0.53 ±0.05 ($R^2=0.754$)

7.3.3.1 The Dissolved organic carbon (DOC) and log of discharge (log Q) relationship

A poor relationship was identified between dissolved organic carbon (DOC) and the log of discharge (log Q) in both the Duchray and Elrig catchments. Similar poor relationships were identified in the 1989-90 study within the same catchments. When these relationships are compared, as shown in Figure 64, it can be observed that the relationship between DOC and log Q has stayed the same in the Duchray and Elrig catchments, but the DOC concentrations have increased. To statistically determine if the relationship between DOC and log Q had changed between the two sampling period, the F-test statistic was calculated using the 1989-90 and 2004-06 data; the calculated F-test statistic (196.59) was greater than the F value of 3.00 in the Duchray catchment and this trend was replicated in the Elrig catchment where the calculated F-test statistic (298.57) was greater than the F value of 3.01, identifying that the relationship between DOC and the log of discharge had changed in both catchments.

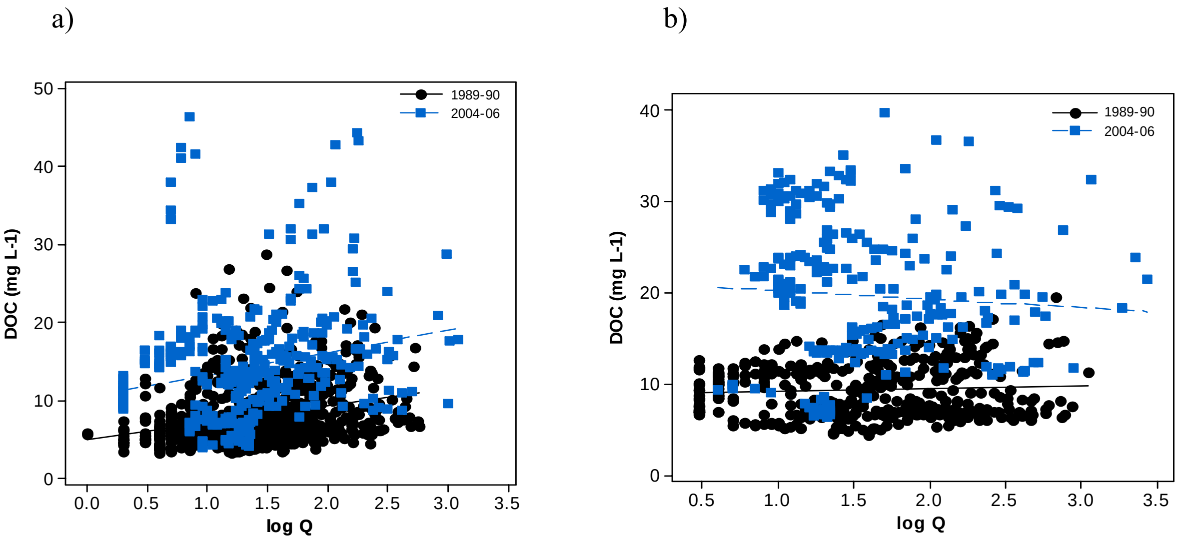
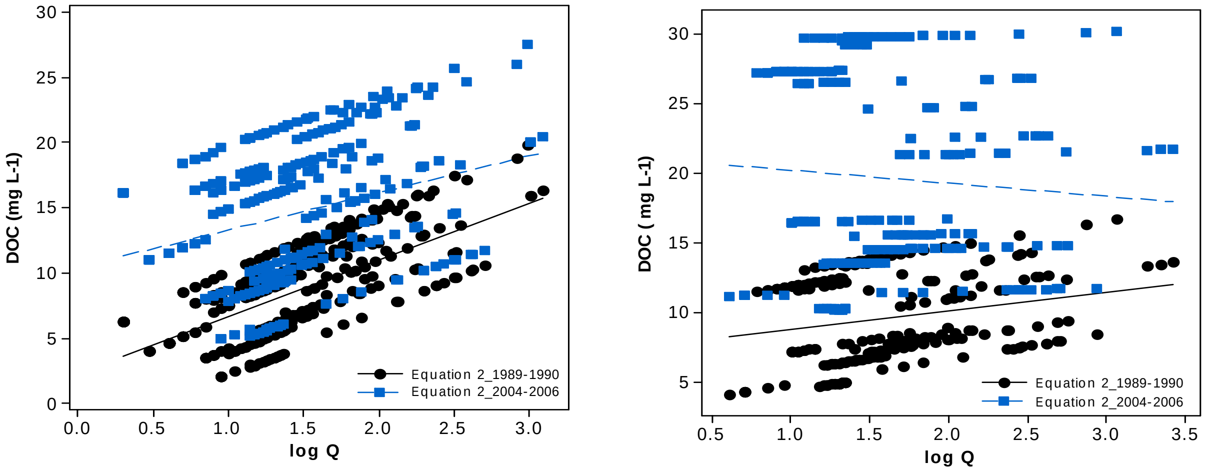


Figure 64: Scatterplot showing the regression relationship between dissolved organic carbon (DOC) (mg L-1) and the log of discharge (log Q), from data collected during 1989-1990 and 2004-2006 in the a) Duchray catchment and b) Elrig catchment.

7.3.3.2 Comparison of the DOC, log Q and sine regression equation

When the regression equations produced for the relationship between DOC as the dependent variable and log Q and sine are compared, in both catchments the intercept and the SI value is much higher. The log Q value is similar for the Duchray but in the Elrig it is slightly negative, but still similar to the 1982-83 value. The regression equations from 1982-83 and 2004-06 predicting DOC concentration, plotted against the log of discharge are shown in Figure 65, where it can be observed that the slope of the regression within the Duchray catchment is again similar during both sampling periods and concentrations have again been estimated to increase. However in the Elrig catchment, the regression line produced from the present study shows a slighty negative relationship between DOC and discharge, although concentrations have again increased in the present study. To statistically determine if the relationship between DOC, log Q and sine had changed between the two sampling period, the F-test statistic was calculated using the 1989-90 and 2004-06 data; the calculated F-test statistic (358.99) was greater than the F value of 3.00 in the Duchray catchment and this trend was replicated in the Elrig catchment where the calculated F-test statistic (1609.95) was greater than the F value of 3.01, identifying that the relationship between DOC, log Q and sine had changed in both catchments.


a)

b)

Figure 65: Scatterplots showing the relationship between the log of discharge (log Q) and DOC concentrations from data collected during 1989-90 and 2004-2006, DOC concentrations were produced using regression equations for a) Duchray catchment using log Q (L s^{-1}) and a seasonal sine index with maximum in August and b) Elrig catchment using log Q (L s^{-1}) and a seasonal sine index with maximum in August.

7.3.3.3 Comparison of the DOC, log Q, sine and number of days since last event regression equation

When the regression equations produced for the relationship between DOC as the dependent variable and log Q, sine and the number of days since a previous storm event are compared, then it can be seen that in both catchments the intercept is much higher. However, the other parameters in the regression equations differ. In the Duchray the log Q, SI and TD were all found to be higher. In the Elrig log Q and TD are now smaller, but SI is now greater. The regression equations from 1982-83 and 2004-06 predicting DOC concentration, plotted against the log of discharge are shown in Figure 66 where it can be observed that the slope of the regression is similar between the two sampling periods in both catchments and DOC concentrations have also increased in both catchments.

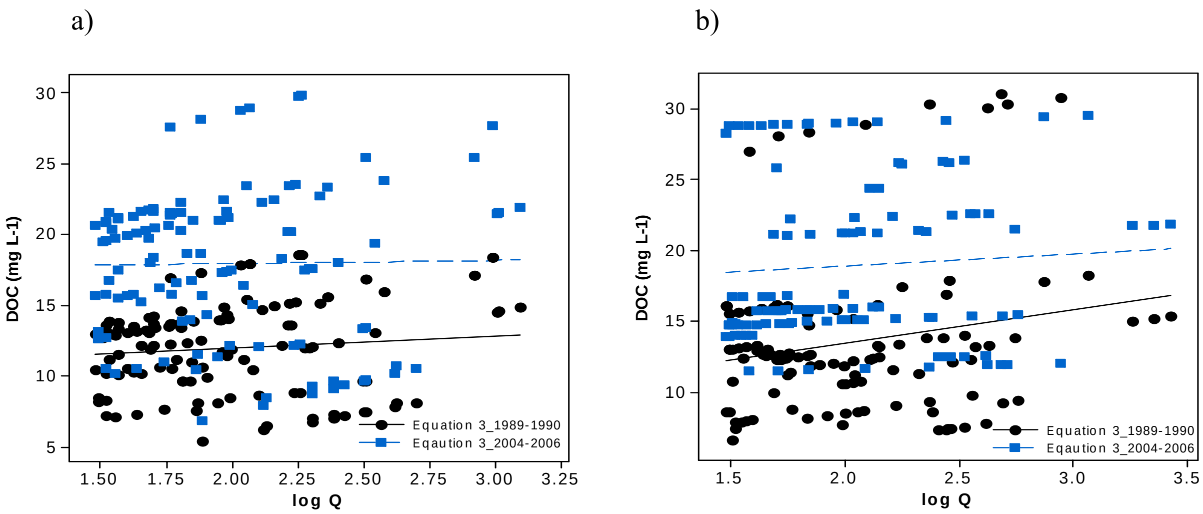


Figure 66: Scatterplots showing the relationship between the log of discharge (log Q) and DOC concentrations from data collected during 1989-1990 and 2004-2006, DOC concentrations were produced using regression equations for a) Duchray catchment using log Q (L s^{-1}), a seasonal sine index with maximum in August and the number of days since the last event and b) Elrig catchment using log Q (L s-^{1}), a seasonal sine index with maximum in August and the number of days since the last event

7.4 Discussion

7.4.1 Modelling DOC concentration in the Ochil Hills catchments

The principal controls of dissolved organic carbon (DOC) concentration were identified within Chapter 4 as temperature, precipitation and soil hydrology. Within Chapter 7, variables have been produced that represented these drivers in terms of both the production (seasonal sine values and 14 day average temperatures) and movement (log of discharge (log Q) and rising or falling stage) of DOC. These variables were successfully used in the previous research (Grieve, 1984a) to model DOC concentrations. When the regression analysis conducted in the previous study was repeated, a strong relationship between DOC and log Q (R^2=0.59) was found within the Ochil Hills catchment. The relationship was improved with the addition of the seasonal sine values variable (R^2=0.78), however the addition of the rising and falling stage variable only improved the relationship slightly (R^2=0.79). In the final equation, when 14 day mean temperatures were used in place of the sine variables, again only a slight improvement in the model was seen (R^2=0.80). When new variables not measured in the previous study (Grieve, 1984a) were used, it was identified that the use of 4 hour average log Q and 1 day average 30cm soil temperatures were strong predictive variables when modelling DOC concentration (R^2=0.88). The regression models produced at the Ochil Hills catchment highlight the importance of precipitation in the movement of DOC to the stream, and the temperature variables used representing the production of DOC within the surrounding catchment, which supports hypothesis 1 of this thesis.

7.4.1.1 Changes in DOC concentration in the Ochil Hills catchment

To achieve the final objective of this thesis to identify how DOC concentrations have changed within the Ochil Hills stream between the two sampling periods (1982-83 and 2004-06), then it was necessary to identify how the relationship between DOC and discharge had changed. To achieve this regression analysis that was conducted during the first sampling period (1982-83) was repeated. When the relationship between DOC and log Q was compared over time, the log Q value within the regression equation had increased, suggesting that in comparison to the previous sampling period, there is now more DOC available for movement from the soil, at the same unit discharge. When the three regression equations produced to model DOC concentration, using seasonal sine values, rising and falling stage and 14 day average temperature were compared to the corresponding regression equation produced during the previous study, then it was observed that there was little change in the intercept value. However, the seasonal sine values and the 14 day average temperature value had decreased in the equations produced during the present sampling period. The F-test statistic confirmed that the relationship between DOC and the log Q and the seasonal sine values had changed over time. Average winter temperatures in the west of Scotland have increased between 1961 and 2004, by 1.31°C (Hulme *et al*., 2002), therefore there is potentially increased DOC production in the winter, and therefore the difference in DOC production between the winter and summer will have decreased, explaining why the seasonal sine value and 14 day average temperature values in the regression equations have decreased. The difference between the sampling periods could more clearly be observed when the DOC modelled using the regression equations were plotted against log Q; a steeper regression slope was observed for the relationship between DOC and log Q for the present sampling period, showing higher DOC concentrations were produced during the same unit discharge as in the previous study. High DOC concentrations were measured during September 2004 and August 2005, which caused the increase in the slope of the regression seen in the 2004-06 data. These peak DOC concentrations measured also altered the fit of the seasonal sine wave to the residuals of the DOC/log Q relationship, as the peak value in the present study was at the beginning of September, however in the previous study the peak was during August. This suggests that the seasons are changing and indeed the growing season in the west of Scotland is now five weeks longer than during the 1960s (Barnett *et al.* 2006).

The increase in DOC concentrations measured in the Ochil Hills catchment over time was small. However, the majority of studies monitoring long term changes in DOC concentrations, have identified significant increases in DOC concentrations in a range of catchments in the UK, over the last two decades (McCartney *et al.* 2003; Harriman *et al*., 2001), and Evans *et al.* (2006) noted a 91% increase in DOC concentration since 1988 in UK lakes and streams monitored in the acid waters monitoring network. Yet, increased DOC concentrations have not been measured in all catchments, for instance of the 198 catchments examined in Worrall *et al.*'s (2004) study, forty five showed no significant increasing trend in DOC concentration and two showed a downward trend. The majority of studies investigating DOC increases have focussed on changes in climate, specifically temperature, and in these studies the measured temperature increases have been determined to only account for a small percentage of the increase in DOC concentration measured, 12% (Worrall *et al*., 2004) or 10-20% (Evans *et al*., 2006). These small increases would account for the increase in DOC concentration measured within the Ochil Hills catchment. In other studies, it has been identified that the reduction in acidic deposition (Evans *et al*., 2006) is increasing the solubility of DOC (Chapman 2005; Andersson 2000) within the soil and therefore increasing the concentrations measured. However in the Ochil Hills catchment, the influence of acidic deposition was limited, because of the geology of the catchment. Andesitic and balsaltic lavas compose 75% of the solid geology of the catchment and the weathering of these rocks produce cations that can exchange with the H^+ ions to neutralise the acidic deposition (Monteith and Evans, 2001). In a previous study at the Ochil Hills catchment (Grieve, 1986), which was performed concurrently with the modelling study between 1982-83, major ions were measured and high mean concentrations of calcium (31.4 mg L^{-1}) and magnesium (4.48 mg L^{-1}) were measured indicating that cation exchange was acting to decrease the effects of acidic deposition within the catchment, and as such the pH of the stream was not acidic (pH 6.4-8.0). It has been identified within the Ochil Hills catchment that DOC concentrations have changed over time, but this increase is limited. However it would appear that increases in temperature are driving this change, supporting hypothesis 2 of this thesis.

7.4.2 Modelling of DOC concentration in the Duchray and Elrig catchments

The principal controls of dissolved organic carbon (DOC) concentration in the Duchray and Elrig catchments were identified within Chapter 5 and 6 as temperature, precipitation and soil hydrology. Within Chapter 7, variables have been produced that represented these drivers in terms of both the production (seasonal sine values) and movement (log of discharge (log Q) and number of days since last storm event (TD)) of DOC. A weak relationship was identified between DOC and the log of discharge (log Q) in the Duchray (R^2= 0.045) and Elrig (R^2= 0.143) catchments. The use of the seasonal sine values greatly improved the model in the Duchray (R^2= 0.483) and Elrig (R^2= 0.796) catchments. A similar relationship was found when the number of days since the last event variable was used in the model for the Duchray (R^2= 0.453) and Elrig (R^2= 0.762) catchments. The difference between the strength of the relationships in the catchments indicates that different drivers are important within the Duchray and Elrig catchments. However, it is perhaps the individual characteristics of the catchments that have resulted in the different relationships. The area of wetland in the Elrig catchment was seen to reduce variability in DOC concentrations in the previous study and the larger percentage of mineral soils within the Duchray catchment were thought to control the release of DOC (Grieve, 1994). This explains why there was little difference in the mean discharge weighted concentration of DOC measured within the two catchments during the previous study (Grieve, 1994) although felling had occurred in the Duchray catchment. In the present study a higher mean discharge weighted concentration of DOC was measured within the Elrig catchment (19.97 mg L^{-1}), than the Duchray catchment (16.7 mg L^{-1}). The differences observed may be due to the limited felling that occurred in the Elrig catchment during 2004-05, as disturbance within catchments have been identified to increase DOC concentrations in other similar catchments (Moore, 1989; Cummins and Farrell, 2003) although not in the Duchray catchment (Grieve, 1994). The regression models produced at the Duchray and Elrig catchment highlights the importance of precipitation in the movement of DOC to the stream, and the temperature variables used representing the production of DOC within the surrounding catchment, which supports hypothesis 1 of this thesis

7.4.2.1 Changes in DOC concentration in the Duchray and Elrig catchments

To achieve the final objective of this thesis to identify how DOC concentrations have changed within the Elrig and Duchray catchments between the two sampling periods (1989-90 and 2004-2006), then it was necessary to identify how the relationship between DOC and discharge had changed. To achieve this regression analysis that was conducted during the first sampling period (1989-90) was repeated and it was found that dissolved organic carbon (DOC) concentrations have increased in the Elrig and Duchray catchment since the previous study was conducted from 1989 to 1990 (Grieve, 1994). In the Duchray catchment the relationship between DOC and log Q had changed, the slope of the regression line remained the same, however higher concentrations of DOC were being measured at the same discharges. Similar trends were observed in the relationship between DOC and log Q, when DOC concentrations were produced using the regression equations using the seasonal sine values and the number of days sine the previous storm event (TD). In the Elrig catchments, concentrations of DOC had also increased, however the slope of the regression line had changed; in the present study a slight negative relationship was identified between DOC and log Q, which was also observed in the regression relationship developed using the seasonal sine values. This relationship may have been produced because of the reduced number of samples collected within the Elrig catchment, as a similar slope of regression was observed, when the number of days since the previous storm event (TD) variable was used to predict DOC concentrations, when only samples taken when discharge was greater than 30 L s^{-1} were used.

The increasing DOC trend that was observed within both catchments, was also identified by Tetzlaff *et al.* (2007) in an analysis of long tern data (>25 years), taken at weekly or fortnightly intervals since 1983, from both catchments. Results of this study shown in Figure 62, confirm that DOC concentrations increased between the previous (1989-1990) and present (2004-2006) sampling periods. It can also be observed that baseflow DOC concentrations are also increasing, specifically in the Elrig, which suggests that factors other than discharge are altering the concentrations of DOC within this catchment.

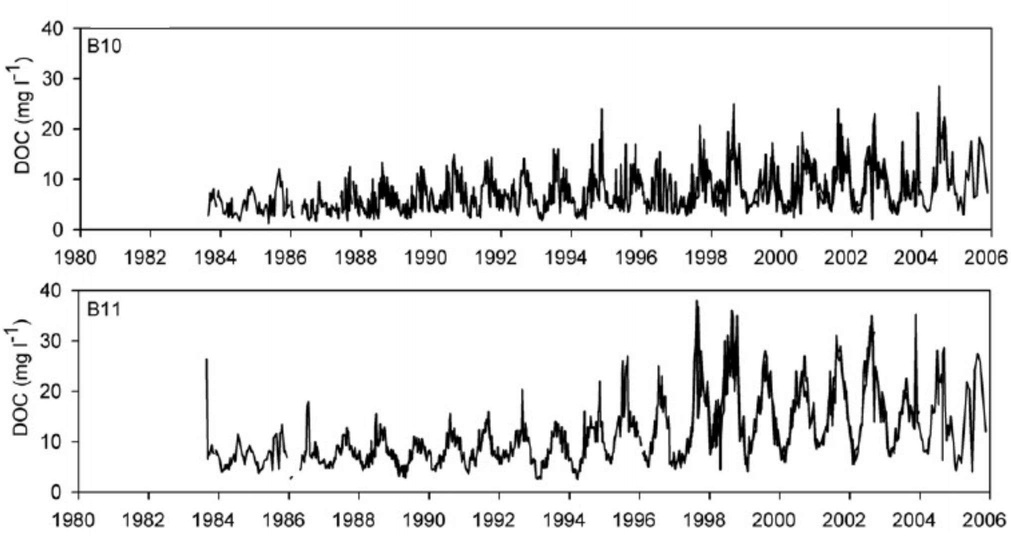


Figure 67: Long term variation in dissolved organic carbon (DOC) in the Duchray (B10) and Elrig (B11) streams (after Tetzlaff *et al.* (Tetzlaff *et al.,* 2007)).

It is suggested that the large increases in DOC concentrations measured within the Duchray and Elrig catchment, cannot be explained by changes in climate alone (Evans *et al.,* 2006; Worrall *et al.,* 2004a). The increases measured are potentially due to reductions in sulphur deposition (Evans *et al.,* 2006), reducing soil acidity and increasing the solubility of DOC (Chapman *et al.,* 2005; Andersson *et al.,* 2000). The Loch Ard area has been identified as an area that has been acidified (Harriman *et al.,* 2001) because of the base poor geology within the catchment, however it has been identified to be recovering as both acidity and xSO_4 concentrations have declined since the early 1970s when the UK emissions of SO_2 were at their highest in the Loch Ard forest (Harriman *et al.,* 2001). This recovery can be observed in Figure 68, where a reduction in acidity can be observed in both catchments. This has potentially resulted in the increased DOC concentration measured in the Duchray and Elrig catchments in combination with rising temperatures as identified in previous studies (Evans *et al.,* 2005), supporting hypothesis 2 of this thesis.

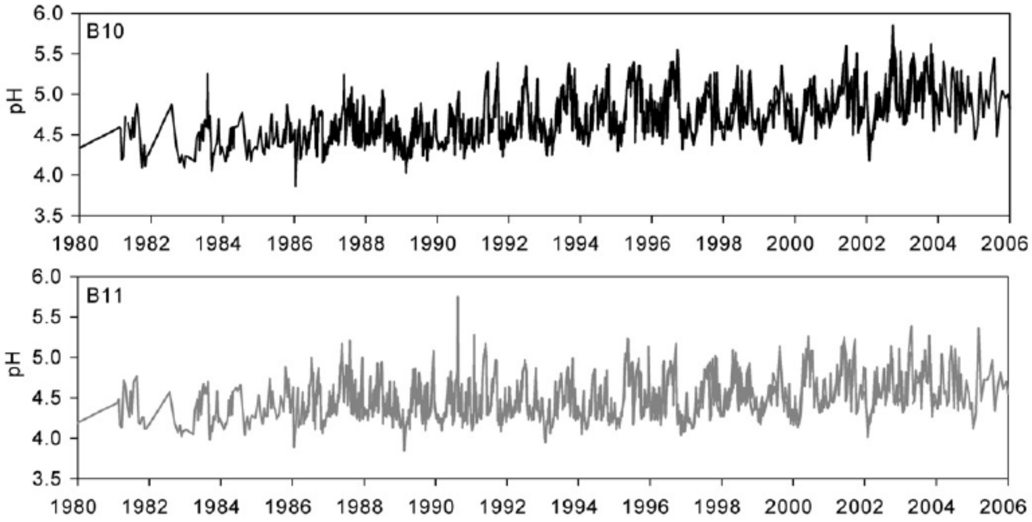


Figure 68: Long term variation in pH in the Duchray (B10) and Elrig (B11) streams (after Tetzlaff *et al*. (Tetzlaff *et al.,* 2007)).

The results from the Loch Ard catchment show that the concentration of DOC has increased, but unlike the Ochil Hills catchment where temperature was driving the change, here it appears that that reduction in acidic deposition is the over riding control. Resulting in a larger increase in DOC concentration in the Loch Ard catchments and supporting hypothesis 3 of this thesis.

Chapter 8 - Conclusions

Dissolved organic carbon (DOC) concentrations have increased over the last 10-20 years, in the moorland and two forest catchment streams monitored within this study, corresponding with widely reported DOC increases in water bodies in the industrialised parts of Europe and North America. This is a worrying trend, as it could reflect increased losses of carbon from peatland carbon stores. The reasons behind the increases in DOC concentration are not yet fully understood, however this study has identified the importance of potential causes which include changes in climate and a reduction in acidic deposition.

The production of models to predict DOC concentrations in this study highlighted the importance of the catchments hydrology in altering DOC concentrations within the streams. A strong DOC/log of discharge relationship within the moorland catchment contrasted with a weak relationship in the two forest catchments. However, the strength of the relationship was generally improved when divided by season in all catchments, showing not only the importance of temperature in the production of DOC, but that the importance of individual drivers differs between catchments. In the Ochil Hills catchment, several models were produced and the best predictive model, used 4 hour average discharge and 1 day average 30cm soil temperatures (R^2= 0.88). In the Duchray and Elrig catchments, discharge and seasonal sine values produced the best models, but the strength of the model was greater in the Elrig (R^2=0.80) than the Duchray (R^2=0.48) catchment. Therefore, when modelling DOC concentrations all aspects of the individual catchment need to be considered, as the difference in the strength of the relationship between the two forest catchments can be explained by the more rapid movement of DOC in the Duchray catchment due to the steeper slopes, and the larger availability of DOC within the Elrig catchment due to its more organic soil.

Comparison of the relationship between DOC and the log Q in the three study catchments identified that DOC concentrations have increased in all catchments. However, the potential causes for these increases differed between catchments. Modelling in the moorland catchment identified an increased availability of DOC within the soil, and a reduction in the difference between winter and summer DOC production, potentially due to increasing temperatures, explaining the small increase in DOC concentration measured within the moorland catchment between the two study periods (1982-83 and 2004-06). In the Duchray and Elrig catchments, a more pronounced change in the relationship between DOC and log Q was observed, with increased DOC concentrations measured at all discharges, when all models produced were compared between the two sampling periods (1989-90 and 2004-06). The increasing trend in DOC concentrations is too large to have been produced by change in temperature alone, and it is suggested that the measured reduction in acidic deposition, has resulted in the increased DOC concentrations measured in the Duchray and Elrig catchments due to their base poor geology.

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Appendix A - Analysis of dissolved organic carbon (DOC) and total nitrogen (TN)

Dissolved Organic Carbon concentrations, were analysed by a Shimadzu Total Organic Carbon (TOC) analyser, using two methods the total carbon - inorganic carbon (TC-IC) method and the non-purgeable organic carbon (NPOC) method. Total nitrogen (TN) concentrations were measured concurrently with both methods of DOC analysis. To ensure the results presented are accurate, analysis of all samples was repeated three times. If the standard deviation (SD) of this repeat analysis exceeds 0.1 and the coefficient of variance (CV) exceeds 2%, then analysis was repeated a further two times. The mean concentration of the sample was then calculated from the three results that meet the SD and CV values

Total carbon - inorganic carbon (TC-IC) method

To determine the total organic carbon (TOC) concentration within the sample, the total carbon (TC) and inorganic carbon (IC) concentrations were measured. The TOC concentration was then calculated, by subtracting the IC value from the TC value.

Principles of total carbon (TC) measurement

A Shimadzu Total Organic Carbon (TOC) analyser measured the total carbon concentration (organic and inorganic) of the sample. The sample is drawn from the vial and is introduced into the combustion chamber, which is filled with an oxidation catalyst and heated to 720°C (when the TOC/TN catalyst is used). Here, the sample is burnt and the TC component forms carbon dioxide. Carrier gas (pure oxygen flowing at a rate of 150 mL/min), then moves the carbon dioxide and other combustion products from the combustion tube to the electronic humidifier, where it is cooled and dehydrated. The carrier gas then moves the sample through a halogen scrubber, which removes chlorine and other halogens, to the non-dispersive infrared (NDIR) gas analyzer, where the carbon dioxide is detected (Shimadzu Corporation , 2001).

Principles of inorganic carbon (IC) measurement

The inorganic carbon component of TOC, refers to the carbon from carbonates, hydrogen carbonates and dissolved carbon dioxide (Shimadzu Corporation , 2001). To determine the concentration of IC within the sample, the sample was drawn into the injection syringe, where it was acidified to pH 3 or lower by the addition of hydrochloric acid (HCL), and then sparged with the carrier gas. The acidification of the sample produces the following reactions, where the carbonates within the sample produce CO_2: -

$$Me_2CO_3 + 2HCL \rightarrow CO_2 + 2MeCl + H_2O$$

$$MeHCO_3 + HCL \rightarrow CO_2 + MeCl + H_2O$$

Where: -

Me = Metal atom e.g. calcium

This carbon dioxide is then volatilized, when the carrier gas sparges the sample within the injection syringe. The IC component, which has now been converted to CO_2, is then detected by the NDIR gas analyser (Shimadzu Corporation , 2001).

Principles of non-purgeable organic carbon (NPOC) measurement

In the NPOC method the sample is acidified to pH 2 or 3, through a 3% acid addition, and sparge gas is bubbled through the sample for 90 seconds to remove the IC component. The TC that remains in the sample is then measured as outlined in the TC method and the resulting concentration is defined as TOC.

Principles of total nitrogen (TN) measurement

The total nitrogen (TN) concentration measured, includes both organic and inorganic nitrogen**.** The total nitrogen (TN) analysis is performed concurrently with the TC and NPOC analysis. However after combustion in the furnace (burning at 720°C), the nitrogen monoxide gas is then moved by the carrier gas to the electronic dehumidifier where it was cooled and de-humidified. It is then detected within the chemiluminescence gas analyser where a peak was generated from which the TN concentration was determined.

Calibration

Calibration curves were produced for each individual analysis (TC, IC, NPOC and TN), prior to analysis of samples. In the production of the calibration curve, two standards and a blank were analysed by the Shimadzu Total Organic Carbon (TOC) analyser. During analysis, the non-dispersive infrared (NDIR) gas or the chemiluminescence gas analyzer, produces an analog detection signal that forms a peak. The area of this peak is then measured by the TOC-control software for the two standards and the blank, to produce the calibration curve. In the production of the calibration curves, the shift to origin function was used, to shift all the points on the calibration line in parallel, to take into account the concentration of TC, IC or TN within the double distilled de-ionised water, blank. The calibration equation, which mathematically expresses the relationship between the peak area and concentration, was then used to determine TC, IC or TN concentrations.

TC Standard Solutions

The TC standard was made by dissolving 2.125 g of potassium hydrogen phthalate ($KC_8H_5O_4$), which was previously dried at 120°C for an hour and cooled in a desiccator in a 1 L volumetric flask made up to the 1 L mark with double deionised water. The TC standard solution was then used to produce the TC/TN mixed standard.

IC Standard Solutions

The IC standard was made using 3.50 g of reagent grade sodium hydrogen carbonate ($NaHCO_3$), dried for two hours in a silica gel dessicator and 4.41 g of sodium carbonate (Na_2CO_3), previously dried for 1 hour at 280-290ºC and cooled in a desiccator. They are both dissolved in a 1 l volumetric flask and made up to the 1 l mark with double deionised water. The IC standard solution was then diluted to produce a range of standards to produce two calibration curves. The first calibration curve, used standards diluted, using double deionised water, to 10, 5 and 0 mg C l^{-1}. The second calibration curve used standards diluted to 100, 50 and 0 mg C l^{-1}.

TN Standard

The TN standard was made using 7.219g of special regeant grade potassium nitrate (KNO_3) dried for 3 hours at 110ºC and cooled in a desiccator. This was then dissolved in a 1L volumetric flask made up to the 1L mark with double deionised water. The TN standard solution is then used to produce the TC/TN mixed standard.

Mixed 100mg/L TC/TN standard Solution

When TC and TN analysis was performed simultaneously, a mixed standard was made to calibrate the TOC analyser. 100ml of each of the prepared 1000 mg l^{-1} TC and standards were introduced into a 1000ml volumetric flask. 25ml of 2M hydrochloric acid was added to the flask, and double deionised water was then added to make up to the 1L mark. The mixed TC/TN standard was used to produce a calibration curve using standards of 100 mg C/N/L and diluted standards using double deionised water to 50 and 0 mg C l^{-1}.

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Appendix B - Measurement of dissolved organic carbon (DOC) using the potassium dichromate oxidation method

Reagents

The reagents used in the measurement of dissolved organic carbon (DOC) concentration using the potassium dichromate oxidation method included: -

Potassium dichromate - 4.9035 g of dried potassium dichromate is dissolved in distilled water and made up to 1000 ml.

Ammonium iron sulphate - 19.6 g of ammonium iron sulphate is dissolved in distilled water, to this 5 ml of concentrated sulphuric acid is added, which is then made up to 1000 ml with distilled water.

Barium diphenylamine sulphonate- 0.16 g of barium diphenylamine sulphonate was dissolved in distilled water and made up to 100 ml with distilled water.

Method of Analysis

50ml of the sample is measured and poured into a conical flask; the sample is placed in an oven and evaporated to dryness at 80°C, overnight. The following day, 10 ml of M/60 potassium dichromate solution (a strong oxidising agent) is added to the flask which is swirled to dissolve the residue, and 20 ml of concentrated sulphuric acid is added, after which it was left to react for 30 minutes. Then 200 ml of distilled water, 10 ml of concentrated orthophosphoric acid and 2ml of barium diphenylamine sulphonate indicator solution are added to the flask. The resulting solution is titrated against M/20 ammonium iron (II) sulphate to a green endpoint, to determine the remaining concentration of potassium dichromate. Samples were also analysed for their chloride concentrations using a Dionex DX120 ion chromatograph.

Calculation of DOC

To calculate the concentration of DOM within the sample, then initially the chemical oxygen demand (COD); the weight of oxygen that is required in the oxidation of any sample containing organic matter (Maciolek 1962), is calculated using equation A-1

$$COD = \frac{(Vb - Vs) \times 8000}{Vol \times Vb}$$ **Equation A-1**

Where

COD = Chemical oxygen demand (mg/L of O_2)

Vb = titre volume of blank

Vs = titre volume of sample

Vol = sample volume

The presence of inorganic chloride in the sample, will affect the accuracy of the final result (Maciolek J.A., 1962), hence this is corrected using equation A-2 and A-3.

Chloride Correction of COD = COD – chloride O.C. **Equation A-2**

Chloride O.C = Chloride O.E. * chloride (mg/L) **Equation A-3**

Where

COD = Chemical Oxygen Demand

Chloride O.C. = Chloride oxygen consumed value

Chloride O.E. = Chloride Oxygen Equivalent (0.226)

The chloride corrected COD is then converted to dissolved organic matter (DOM) by dividing the oxygen equivalent value of 1.44. To determine the concentration of DOC within the sample then this value is divided by two, as 50% of the DOM is assumed to be carbon (Grieve, 1984a)

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